# HAROLD H. SCHOBERT Chemistry of Fossil Fuels and Biofuels

CAMBRIDGE

## **Chemistry of Fossil Fuels and Biofuels**

Focusing on today's major fuel resources – ethanol, biodiesel, wood, natural gas, petroleum products, and coal – this book discusses the formation, composition and properties of the fuels, and the ways in which they are processed for commercial use. The book examines the origin of fuels through natural processes such as photosynthesis and the geological transformation of ancient plant material; the relationships between their composition, molecular structures, and physical properties; and the various processes by which they are converted or refined into the fuel products appearing on today's market. Fundamental chemical aspects such as catalysis and the behaviour of reactive intermediates are presented, and global warming and anthropogenic carbon dioxide emissions are also discussed. The book is suitable for graduate students in energy engineering, chemical engineering, mechanical engineering, and chemistry, as well as for professional scientists and engineers.

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## **Chemistry of Fossil Fuels and Biofuels**

HAROLD SCHOBERT

The Pennsylvania State University and North-West University



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"The book is a welcome modern update to the available literature regarding the genesis, characteristics, processing and conversion of fossil and bio-derived fuels. Its comprehensive coverage of the chemistry involved with each of these aspects makes it an important source for upper-level undergraduates, graduate students, and professionals who need a strong understanding of the field. It is an interesting read for anyone who really wants to understand the nature of fuels."

## Robert G. Jenkins, University of Vermont

"There is no other book like this in field of energy science. It is the perfect introduction to the topic; but Professor Schobert has packed so much in, that it is just as much a valuable reference for more experienced professionals. It touches on all aspects of fuel formation, transformation and use as well as strategies for managing the end product, carbon dioxide. I will be using it as a text in my own teaching to both senior undergraduate and graduate students."

## Alan L. Chaffee, Monash University, Australia

"This is an excellent reference for the student of modern fuel science or the practitioner wishing to sharpen their 'big-picture' understanding of the field. The book offers a seasoned balance between technical rigor and readability, providing many helpful references for the reader interested in further study. I found the text engaging and enlightening, with the end-of-chapter notes a particularly thought-provoking and entertaining bonus."

Charles J. Mueller, Sandia National Laboratories

## Contents

	Preface	page xv
	Acknowledgments	xvii
	Acknowledgments for permissions to use illustrations	xviii
1	Fuels and the global carbon cycle	1
	Notes	8
2	Catalysis, enzymes, and proteins	10
	2.1 Catalysis	10
	2.2 Proteins	11
	2.3 Enzymes	13
	Notes	17
3	Photosynthesis and the formation of polysaccharides	19
	3.1 Water splitting in photosynthesis	20
	3.2 Carbon dioxide fixation	24
	3.3 Glucose, cellulose, and starch	27
	Notes	32
4	Ethanol	35
	4.1 Fermentation chemistry	35
	4.2 Commercial production of ethanol via fermentation	38
	4.3 Ethanol as a motor vehicle fuel	42
	4.4 Issues affecting possible large-scale production of fuel ethanol	47
	4.5 Cellulosic ethanol	48
	Notes	49
5	Plant oils and biodiesel	53
	5.1 Biosynthesis of plant oils	53
	5.2 Direct use of vegetable oils as diesel fuel	57
	5.3 Transesterification of plant oils	59
	5.4 Biodiesel	62
	Notes	66

6	Composition and reactions of wood	69
	6.1 Wood combustion	78
	6.2 Wood pyrolysis	79
	6.2.1 Charcoal	79
	6.2.2 Methanol	81
	6.3 Wood gasification	82
	6.4 Wood saccharification and fermentation	83
	Notes	84
7	Reactive intermediates	87
	7.1 Bond formation and dissociation	87
	7.2 Radicals	89
	7.2.1 Initiation reactions	89
	7.2.2 Propagation reactions	91
	7.2.3 Termination reactions	94
	7.3 Radical reactions with oxygen	95
	7.4 Carbocations	97
	7.5 Hydrogen redistribution	100
	Notes	101
8	Formation of fossil fuels	103
	8.1 Diagenesis: from organic matter to kerogen	104
	8.2 Catagenesis: from kerogen to fossil fuels	109
	8.3 Catagenesis of algal and liptinitic kerogens	111
	8.4 Catagenesis of humic kerogen	117
	8.5 Summary	127
	Notes	128
9	Structure-property relationships among hydrocarbons	132
	9.1 Intermolecular interactions	132
	9.2 Volatility	134
	9.3 Melting and freezing	142
	9.4 Density and API gravity	145
	9.5 Viscosity	148
	9.6 Water solubility	151
	9.7 Heat of combustion	152
	9.8 The special effects of aromaticity	156
	Notes	158
10	Composition, properties, and processing of natural gas	161
	10.1 Gas processing	164
	10.1.1 Dehydration	164
	10.1.2 Gas sweetening	166

		10.1.3 Separation of $C_2^+$ hydrocarbons	168
	10.2	Natural gas as a premium fuel	170
	Note	2S	171
11	Comp	position, classification, and properties of petroleum	174
	11.1	Composition	174
		11.1.1 Alkanes	174
		11.1.2 Cycloalkanes	175
		11.1.3 Aromatics	177
		11.1.4 Heteroatomic compounds	179
		11.1.5 Inorganic components	180
	11.2	Classification and properties of petroleums	181
		11.2.1 API gravity	181
		11.2.2 Carbon preference index	181
		11.2.3 Age-depth relationships	182
		11.2.4 Composition relationships	183
	11.3	1 , ,	187
	Note	S	189
12	Petro	leum distillation	192
	12.1	Desalting	193
	12.2	Principles of distillation	194
	12.3	Refinery distillation operations	198
		12.3.1 Atmospheric-pressure distillation	198
		12.3.2 Vacuum distillation	199
	12.4	1 1	200
		12.4.1 Gasoline	200
		12.4.2 Naphtha	201
		12.4.3 Kerosene	201
		12.4.4 Diesel fuel	202
		12.4.5 Fuel oils	202
		12.4.6 Lubricating oils	203
		12.4.7 Waxes	203
	Note	12.4.8 Asphalt	204 204
10	Uster		000
13		ogeneous catalysis	206
	13.1	Catalytic materials	207
		13.1.1 The active species	207
		13.1.2 The support	207
		13.1.3 The promoter	209
	12.2	13.1.4 Preparation	209
	13.2	Adsorption on catalyst surfaces	210
	13.3	Mechanisms of catalytic reactions	216

	13.4	Measures of catalyst performance	217
	13.5	Surface effects on catalysts	219
	Note	s	221
14	Catal	ytic routes to gasoline	224
	14.1	Gasoline combustion	224
	14.2	Specifications and properties of gasoline	229
		Refinery routes to enhanced yield and quality	231
	14.4	Alkylation and polymerization	232
	14.5	Catalytic cracking	234
		14.5.1 Cracking catalysts	235
		14.5.2 Cracking reactions	241
		14.5.3 Practical aspects	243
	14.6	5 6	245
		14.6.1 Reforming catalysts	245
		14.6.2 Reforming reactions	246
		14.6.3 Practical aspects	249
	14.7	Methanol to gasoline	251
	Note	8	253
15	Middl	le distillate fuels	256
	15.1	Middle distillate fuel products	256
		15.1.1 Kerosene	256
		15.1.2 Jet fuel	256
		15.1.3 Diesel fuel	260
		15.1.4 Fuel oils	265
	15.2	Hydroprocessing	266
		15.2.1 Hydrodesulfurization	267
		15.2.2 Hydrodenitrogenation	272
		15.2.3 Hydrodemetallation	273
		15.2.4 Hydrofining	273
		15.2.5 Hydrocracking	274
		15.2.6 Hydrogenation	276
		15.2.7 Sources of hydrogen	277
	Note	S	278
16	Thern	nal processing in refining	281
	16.1	Thermal cracking	281
	16.2	Visbreaking	284
	16.3	Coking processes	286
		16.3.1 Delayed coking	287
		16.3.2 Fluid coking and Flexicoking	292
	Note	S	293

Composition, properties, and classification of coals	295
17.1 Classification of coal by rank	295
17.2 The caking behavior of bituminous coals	298
17.3 Elemental composition	299
17.4 The macromolecular structures of coals	306
17.5 Coals as heterogeneous solids	312
17.6 Physical properties	314
Notes	320
The inorganic chemistry of coals	323
18.1 The origin of inorganic components in coals	324
18.2 Inorganic composition of coals	324
18.3 Minerals in coals and their reactions	326
18.4 Coal cleaning	329
18.5 Behavior of inorganic components during coal utilization	334
Notes	340
Production of synthesis gas	342
19.1 Steam reforming of natural gas	342
19.2 Partial oxidation of heavy oils	344
19.3 Coal and biomass gasification	345
19.3.1 Fundamentals of the carbon-steam and related reactions	346
19.3.2 Coal gasification processes	352
19.3.3 Fixed-bed gasification	354
19.3.4 Fluidized-bed gasification	356
19.3.5 Entrained-flow gasification	357
19.3.6 Underground coal gasification	359
19.3.7 Biomass gasification	360
Notes	361
Gas treatment and shifting	363
20.1 Gas clean-up	363
20.2 Acid gas removal	365
20.3 The water gas shift	371
Note	373
Uses of synthesis gas	375
21.1 Fuel gas	375
21.2 Methanation	375
21.3 Methanol synthesis	378
21.4 Fischer–Tropsch synthesis	381
21.5 Kölbel reaction	389
	<ul> <li>17.1 Classification of coal by rank</li> <li>17.2 The caking behavior of bituminous coals</li> <li>17.3 Elemental composition</li> <li>17.4 The macromolecular structures of coals</li> <li>17.5 Coals as heterogeneous solids</li> <li>17.6 Physical properties</li> <li>Notes</li> <li>The inorganic chemistry of coals</li> <li>18.1 The origin of inorganic components in coals</li> <li>18.2 Inorganic composition of coals</li> <li>18.3 Minerals in coals and their reactions</li> <li>18.4 Coal cleaning</li> <li>18.5 Behavior of inorganic components during coal utilization</li> <li>Notes</li> <li>Production of synthesis gas</li> <li>19.1 Steam reforming of natural gas</li> <li>19.2 Partial oxidation of heavy oils</li> <li>19.3 Coal and biomass gasification</li> <li>19.3.1 Fundamentals of the carbon-steam and related reactions</li> <li>19.3.2 Coal gasification processes</li> <li>19.3 Fixed-bed gasification</li> <li>19.3.5 Entrained-flow gasification</li> <li>19.3.6 Underground coal gasification</li> <li>19.3.7 Biomass gasification</li> <li>19.3.7 Biomass gasification</li> <li>19.3.7 Biomass gasification</li> <li>19.3.7 Biomass gasification</li> <li>19.3.7 Hewater gas shift</li> <li>Note</li> <li>Uses of synthesis gas</li> <li>21.1 Fuel gas</li> <li>21.1 Fuel gas</li> <li>21.2 Methanation</li> <li>21.3 Methanation</li> <li>21.3 Methanation</li> </ul>

	21.6 Oxo synthesis	390
	21.7 Gas to liquids	391
	21.8 The potential of synthesis gas chemistry	392
	Notes	393
22	Direct production of liquid fuels from coal	396
	22.1 Pyrolysis	396
	22.2 Solvent extraction	398
	22.3 Direct coal liquefaction	402
	22.3.1 Principles	402
	22.3.2 Direct liquefaction processing	406
	Notes	413
23	Carbonization and coking of coal	415
	23.1 Thermal decomposition of coals	415
	23.2 Low- and medium-temperature carbonization	417
	23.3 The special case of bituminous coals	418
	23.4 Chemistry of coke formation	420
	23.5 Industrial production of metallurgical coke	426
	Notes	432
24	Carbon products from fossil and biofuels	435
	24.1 Activated carbons	435
	24.2 Aluminum-smelting anodes	440
	24.3 Carbon blacks	443
	24.4 Graphites	445
	24.4.1 Natural graphite	445
	24.4.2 Graphitization processes	446
	24.4.3 Electrodes	447
	24.4.4 High-density isotropic graphites	449
	Notes	450
25	Carbon dioxide	453
	25.1 Carbon capture and storage	455
	25.1.1 Algae	455
	25.1.2 Biochar	457
	25.1.3 Chemical uses of $CO_2$	459
	25.1.4 Coalbed methane recovery	460
	25.1.5 Enhanced oil recovery	461
	25.1.6 Mineral carbonation	462
	25.1.7 Photocatalysis	464

	25.1.8	Underground injection	466
	25.1.9	Urea synthesis	467
25.2	Conclu	usions	468
Note	s		469
Index			472

## Preface

About twenty years ago I wrote a short book, *The Chemistry of Hydrocarbon Fuels*<sup>\*</sup>, that was based on lectures I had been giving at Penn State University for a course on Chemistry of Fuels. In the years since, that book has long been out of print, and the energy community has seen a significant increase in interest in biofuels, and concern for carbon dioxide emissions from fuel utilization. It seemed time, therefore, for a new book in the area. While this present book owes much to the earlier one, the changes are so extensive that it is not simply a second edition of its predecessor, but merits a new title and new organization of chapters.

The life cycle of any fuel begins with its formation in nature, followed by its harvesting or extraction. Many fuels then undergo one or more processes of refining, upgrading, or conversion to improve their properties or to remove undesirable impurities. Finally, the fuel is put to use, usually in a combustion process, but sometimes by further conversion to useful materials such as carbon products or polymers. *Chemistry of Fossil Fuels and Biofuels* focuses primarily on the origins of fuels, their chemical constitution and physical properties, and the chemical reactions involved in their refining or conversion. Most fuels are complex mixtures of compounds or have macro-molecular structures that are, in some cases, ill-defined. But that does not mean that we throw away the laws of chemistry and physics in studying these materials. The composition, molecular structures, and properties of fuels are not some curious, random outcome of nature, but result from straightforward chemical processes. Any use of the fuels necessarily involves breaking and forming chemical bonds.

This book has been written for several potential audiences: those who are new to the field of fuel and energy science, especially students, who seek an introduction to fuel chemistry; practicing scientists or engineers in any field who feel that some knowledge of fuel chemistry would be of use in their activities; and fuel scientists who have been specializing in one type of fuel but who would like to learn about other fuels. I have presumed that the reader of this book will have had an introductory course in organic chemistry, so is familiar with the basic principles of structure, nomenclature, and reactivity of functional groups. I have also presumed that the reader is familiar with aspects of the descriptive inorganic chemistry of the major elements of importance in fuels, and with some of the basic principles of physical chemistry. As a textbook, this book would therefore be suitable for third- or fourth-year undergraduates or first-year graduate students in the physical sciences or engineering. However, anyone with some elementary knowledge of chemistry and who is willing to refer to other appropriate texts as needed could certainly derive much from this book.

Our civilization once relied almost entirely on biomass fuel (wood) for its energy needs. Then, for about two centuries, the fossil fuels – coal, oil, and natural gas – have dominated the energy scene. In recent decades biomass has experienced increasing interest – a revival of interest in wood, as well as ethanol and biodiesel. Anything that we do in daily life requires use of energy, and, in most parts of the world, much of that energy derives from using fossil or biofuels. Despite the critical importance of fuels, few, if any, texts in introductory chemistry or organic chemistry give more than passing mention to these resources. So, I hope that this book might also be of use to chemists or chemical engineers curious to learn about new areas.

This book does not intend, nor pretend, to provide encyclopedic coverage of fuel formation or of refining and conversion processes. At the end of each chapter I have provided a number of suggested sources for those wishing to probe further. The material in the book is the distillation of having taught Chemistry of Fuels at least twenty times to students in fuel science, energy engineering, and chemical engineering. The course has changed somewhat each year, incorporating student feedback as appropriate. The person using this book, either as a textbook or for self-study, should become equipped with enough knowledge then to follow his or her interests with confidence in the professional journals or monographs in the field.

\*The Chemistry of Hydrocarbon Fuels, London, Butterworths, 1990.

## Acknowledgments

I could not have done this without the help and support of my dear wife Nita, who assisted in many, many ways. This book has been developed from more than twenty years' worth of notes for a course, Chemistry of Fuels, that I taught at Penn State University. Every year I started over again making entirely new notes for the lectures. My good friend and colleague, Omer Gül, provided invaluable assistance in converting many of my hand-drawn sketches, used off and on for years, into diagrams for this book. Two staff assistants, Carol Brantner and Nicole Arias, typed some of the versions of hand-written notes and created some of the diagrams. Their work was of great help in pulling the manuscript together. Lee Ann Nolan and Linda Musser, of the Fletcher Byrom Earth and Mineral Sciences Library at Penn State, helped in tracking down information, particularly biographical sketches of fuel scientists. I am also indebted to the staff of the Shakopee branch of the Scott County (Minnesota) Library, who made me welcome and provided a quiet room to work on visits to Minnesota. Many friends and colleagues at Penn State, especially Gary Mitchell and Caroline Clifford, helped in many different ways to provide information or ideas. Professor Christien Strydom, Director of the School of Physical and Chemical Sciences, North-West University, Potchefstroom, South Africa, helped by providing office space and computer access, as well as many splendid discussions. Many other friends at North-West and at Sasol provided assistance in various ways as well. Mohammad Fatemi, President of Middle East PetroChem Engineering and Technology, generously provided the software used to create the chemical structures and reactions. The two people at Cambridge University Press with whom I have worked, Michelle Carey and Sarah Marsh, deserve thanks for their long-suffering perseverance that would make Job seem a pretty impatient fellow. Finally, special thanks are due to the generations of students in Chemistry of Fuels, whose comments and suggestions were actually listened to, and often useful. Despite all this help, which I am very pleased to acknowledge and thank, any mistakes are my own.

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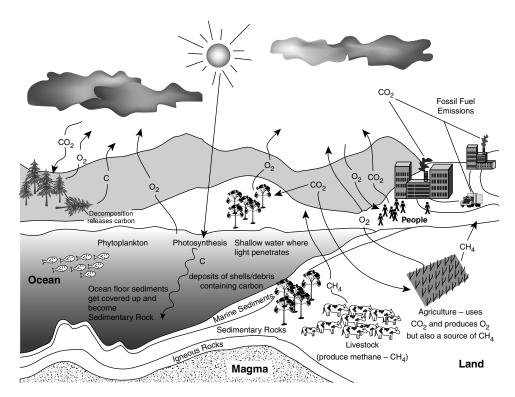
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Fuels are substances that are burned to produce energy. In many practical situations, it can be advantageous first to carry out one or more processing steps on a fuel before it is burned. This might be done to improve the yield of the fuel from its source, to improve the performance of the fuel during combustion, or to mitigate potential environmental problems resulting from using the fuel. Examples include processes to enhance the yield of gasoline from petroleum, to improve gasoline performance in engines, and to convert solid coal into cleaner gaseous or liquid fuels. Some fuels, particularly natural gas and petroleum, also serve as important feedstocks for the organic chemical industry, for producing a host of useful materials. So, fuels can be used in at least three different ways: burned directly to release thermal energy; chemically transformed to cleaner or more convenient fuel forms; or converted to non-fuel chemicals or materials. These uses might appear quite different at first sight, but all have in common the making and breaking of chemical bonds and transformation of molecular structures. The ways in which we use fuels, and their behavior during conversion or utilization processes, necessarily depend on their chemical composition and molecular structure.

The world is now in a transition state between an energy economy that, in most nations, has an overwhelming dependence on petroleum, natural gas, and coal, to a new energy economy that will be based heavily on alternative, renewable sources of energy, including fuels derived from plants. This book covers both. The dominant focus is on wood, ethanol, and biodiesel among the plant-derived fuels, and on coal, petroleum, and natural gas as traditional fuels. If we were to assemble a collection of examples of each, at first sight they would appear to be wildly different. Natural gas, a transparent, colorless gas, commonly contains more than ninety percent of a single compound, methane, at least as delivered to the user. Ethanol, a transparent, volatile, low-viscosity liquid, is a single compound. Petroleum is a solution of several thousand individual compounds. Depending on its source, the color, viscosity, and odor can be very variable. Biodiesel, a lightly colored, moderate viscosity liquid, contains only perhaps a half-dozen individual compounds. Wood, a heterogeneous solid, is usually of light color, but varies in density, hardness, and color, depending on its source. Coals usually are black or brown heterogeneous solids of ill-defined and variable macromolecular structure.

Despite these apparent differences, there are two very important points of commonality. First, all of these fuels occur directly in nature or are made from materials that occur in nature. The second point becomes apparent when we consider the chemical compositions of representative samples, see Table 1.1. **Table 1.1** Chemical compositions, in weight percent, of representative samples of the major fuels covered in this book. The data for wood and coal do not include moisture that might be present in these materials, or ash-forming inorganic constituents.

	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur
Biodiesel	76	13	11	0	0
Coal, bituminous	83	5	8	1	3
Ethanol	52	13	35	0	0
Natural gas	76	24	0	0	0
Petroleum	84	12	1	1	2
Wood, pine	49	6	45	0	0

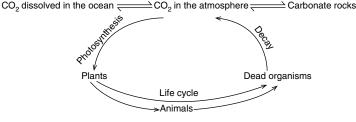


**Figure 1.1** The global carbon cycle, one of the major developments in the earth sciences, allows us to account for the distribution of carbon among the atmosphere, biosphere, and geosphere, and account for the interchange of carbon.

In every case the predominant element, on a mass basis, is carbon. These two points establish a starting place for a study of the chemistry of fuels: the transformations of carbon in natural processes. We will see also that all of these have something else in common – they represent stored solar energy.

The transformations of carbon in nature are conveniently summarized in a diagram of the global carbon cycle, see Figure 1.1.

The global carbon cycle establishes the fluxes of carbon among various sources that introduce carbon into the total environment, and among sinks, which remove or



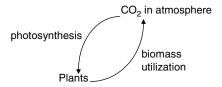
**Figure 1.2** This simplified sketch of the global carbon cycle focuses on processes of particular interest in fuel chemistry. Atmospheric carbon dioxide is incorporated into plants by photosynthesis. The life cycle of living organisms terminates in decay, which returns the carbon to the atmosphere as  $CO_2$ .

sequester carbon. An understanding of the directions of flow and annual fluxes among the sources and sinks has become especially important in recent decades, with increasing concern and focus on atmospheric carbon dioxide concentration and its consequence for global climate change. The world can be thought of as consisting of: the atmosphere; the hydrosphere, dominated by the global ocean; the lithosphere, the crust and upper mantle of solid Earth; and the biosphere, living organisms on, and in, Earth. For the purpose of fuel chemistry, Figure 1.1 can be simplified to the cyclic process of Figure 1.2.

Two equilibria of atmospheric carbon dioxide with natural systems will henceforth be neglected: incorporation of carbon dioxide into carbonate rocks and its release when these rocks are transformed or destroyed; and dissolution of carbon dioxide into the ocean, or its coming back out of solution. Both processes have great importance in the global carbon cycle, but neither has a significant role in formation and use of fuels.

In principle one can start at any point in a cycle and work through it, eventually to return to the start. For this simplified global carbon cycle (Figure 1.2), the atmosphere makes the most convenient starting point. A single compound, carbon dioxide, represents 99.5% of the carbon in the atmosphere (though  $CO_2$  itself is a minor component of the atmosphere, about 0.035% by volume). Green plants remove carbon dioxide from the atmosphere by the process of photosynthesis. The energy in sunlight drives photosynthesis, hence the prefix "photo." (Chapter 2 discusses the chemical details of photosynthesis.) Arguably, photosynthesis is the most important chemical reaction on the planet. Though some life forms do not depend in some way on photosynthesis [end note A], the majority certainly do. Almost all living organisms either use photosynthesis. Our food consists of plants, or of parts of animals that themselves ate plants. Direct use of plants (e.g. wood) or plant-derived substances (e.g. ethanol and biodiesel) as fuels means that we utilize the solar energy accumulated in the plants during their growth.

Plants proceed through their life cycles and eventually die, or might be eaten by animals that, in turn, live through their life cycles and die [B]. The convenient euphemism "organic matter" denotes the accumulated remains of dead plants and animals. Eventually, organic matter decays, usually as a result of action of aerobic bacteria, releasing its carbon back to the atmosphere as carbon dioxide and closing the carbon cycle. The decay process is responsible for the fact that dead organisms disappear from the environment [C]. On a walk in a forest, for example, we do not wade hip-deep in the



**Figure 1.3** Use of biofuels represents a "short-circuit" in the global carbon cycle.  $CO_2$  produced by burning biofuels is removed from the atmosphere by photosynthesis when the next crop of biomass is grown. In principle there should be no long-term net increase in atmospheric concentrations of  $CO_2$ .

accumulated fallen leaves from decades' worth of autumns – leaves from years past are gone because they have decayed.

Photosynthesis converts atmospheric carbon dioxide to glucose [D]:

$$6 \operatorname{CO}_2 + 6 \operatorname{H}_2 \operatorname{O} \to \operatorname{C}_6 \operatorname{H}_{12} \operatorname{O}_6 + 6 \operatorname{O}_2.$$

Glucose is an example of a simple sugar. Its molecular formula could be rewritten as  $C_6(H_2O)_6$  as if it were some sort of compound of carbon and water. The apparent compositional relationship of sugars to a hydrated form of carbon gives the name of this class of compounds – carbohydrates. These sugars play an important role in the biochemistry of plants, acting as an energy source and chemical starting material for the biosynthesis of many other compounds involved in the life processes of the plant. Although the net equation for photosynthesis appears to be fairly simple, the chemistry of photosynthesis is vastly more complicated than implied by this simple equation. Unraveling the chemistry of photosynthesis. The evolution of photosynthetic organisms about three billion years ago allowed oxygen to accumulate in the atmosphere; that in turn made possible the development of life forms that utilize oxygen (including us).

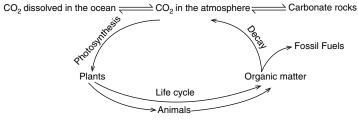
Any organism can consist of hundreds, thousands, possibly tens of thousands of individual chemical components. Decay of accumulated organic matter involves the oxidation reactions of these thousands of compounds. For simplicity, though, consider the oxidative decay of glucose:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O.$$

It can be seen by inspection that an attempt to sum the photosynthesis and decay reactions would result in all terms canceling, i.e. no net output, and the cycle is indeed closed,

$$\frac{6 \operatorname{CO}_2 + 6 \operatorname{H}_2 \operatorname{O} \to \operatorname{C}_6 \operatorname{H}_{12} \operatorname{O}_6 + 6 \operatorname{O}_2}{\underline{\mathrm{C}}_6 \operatorname{H}_{12} \underline{\mathrm{O}}_6} \pm \underline{6 \operatorname{O}_2} \to \underline{6 \operatorname{CO}}_2 \pm \underline{6 \operatorname{H}}_2 \underline{\mathrm{O}},$$
$$\operatorname{net} = 0.$$

At some point very early in human evolution, roughly a million years ago, our ancestor *Homo erectus* learned to burn plants as a source of heat for comfort and for cooking, and likely too in the early development of smelting metals and firing pottery. Grasses and wood were probably the earliest fuels of choice. Sometimes it can be more useful to take only portions of plants, such as the oils used for energy storage in seeds or nuts, for conversion to fuels. Regardless, organisms harvested for use as energy sources represent biomass energy. Fuels made from components of such organisms can be called biofuels. Use of biofuels represents a "short circuit" of the global carbon cycle, see Figure 1.3.



**Figure 1.4** Formation of fossil fuels is a "detour" in the global carbon cycle. About one percent of accumulated organic matter does not decay, but is preserved in the Earth, where a succession of biochemical and geochemical processes transforms the organic matter to fossil fuels.

Most of the focus on biomass energy and biofuels is on plants or plant-derived materials. In part, this is because of the vastly greater mass of plant material available, compared to animals. However, in the developing world, animal dung has been, and still is, dried and used as fuel; animal fat, lard, offers a superb replacement for petroleum-derived fuel oils. Two major considerations drive the current interest in biofuels: First, in principle, biofuels are renewable. For instance, a crop of soybeans harvested this year for production of biodiesel fuel could be regrown next year to produce more biodiesel, and again the year after that, and on and on. Second, again in principle, biofuels have no net impact on atmospheric carbon dioxide; i.e. they are said to be  $CO_2$ -neutral. The amount of  $CO_2$  released by burning a biofuel would be absorbed from the atmosphere during the growth of next year's crop. Both considerations can be challenged in practice. Concerns can be raised about prospects of soil depletion and about the danger of long-term reliance on monocultures. Over the whole life cycle of a biofuel, petroleum and natural gas would probably be used in farming and transportation of the biomass, and in its processing. Despite these concerns, biofuels enjoy both increasing public interest and increasing use.

Currently, though, the mainstay of the energy economy in industrialized nations is energy from coal, petroleum, and natural gas. In the United States, about half of the electricity used is produced in generating plants that burn coal. All of the coke used as fuel and reducing agent in iron-making blast furnaces is made from coal. Natural gas dominates for home heating, except in all-electric homes, and is growing in importance in electricity generation. About 98% of the transportation energy comes from petroleum products. Oil sands, especially those in Canada, are rapidly increasing in importance. Nothing in Figure 1.2, however, accounts for the world's enormous deposits of coal, petroleum, natural gas, oil sands, and oil shales. Multiple lines of evidence, especially for coals and petroleum, show that they derived from once-living organisms. This evidence is discussed in Chapter 8. Because these substances derive from organisms, commonly they are referred to as fossil fuels, from the definition of a fossil as being a remnant of past life preserved in the Earth's crust. Fossil fuels occur because the decay process is not perfectly effective. Some 98–99% of accumulated organic matter indeed decays as indicated in Figure 1.2. The remaining small fraction is preserved against decay, and, over geological time, turns into the materials that we recognize today as the fossil fuels. Formation of fossil fuels can be considered as a detour in the global carbon cycle, see Figure 1.4.

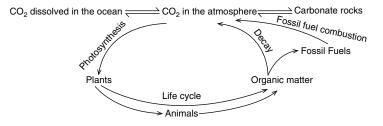


Figure 1.5 Combustion of fossil fuels completes the cycle, releasing the carbon stored in the fuels into the atmosphere as  $CO_2$ .

Thus the origin of the vast deposits of fossil fuels on which we depend so much for our energy economy lies in the fact that a seemingly simple reaction – decay – goes "only" 98–99% to completion. Since the fossil fuels derive from once-living plants that had accumulated energy from sunlight, fossil fuels themselves represent a reservoir of stored solar energy.

However, Figure 1.4 is not complete. Even if <1% of the carbon proceeded through the detour to fossil fuels, running the cycle enough times eventually would result in all the carbon being locked up in fossil fuels. The missing link in Figure 1.4 is the eventual fate of the fossil fuels: they are extracted from the Earth and burned.

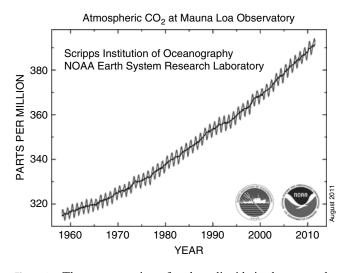
Burning fossil fuels (Figure 1.5) inevitably liberates carbon dioxide. Combustion of methane, the dominant ingredient of natural gas, provides an example:

$$\mathrm{CH}_4 + 2\,\mathrm{O}_2 \rightarrow 2\,\mathrm{H}_2\mathrm{O} + \mathrm{CO}_2.$$

For the global carbon cycle to be at steady state, the rates of removing  $CO_2$  from the atmosphere and adding it to the atmosphere must be equal. The important step for  $CO_2$  removal is photosynthesis.  $CO_2$  returns to the atmosphere from burning biomass or biofuels, decay of organic matter, and burning fossil fuels. When the flux of carbon dioxide into the atmosphere exceeds the flux of carbon into the sinks, concentration of  $CO_2$  in the atmosphere necessarily must increase. A wealth of solid evidence shows that atmospheric  $CO_2$  has been increasing for some time, Figure 1.6 being an example. Carbon fluxes from the sources are indeed outrunning fluxes back into the sinks.

In recent decades, multiple, independent observations from geology, meteorology, and biology show that profound changes are occurring on the planet. These observations include partial melting of the polar ice caps, shrinkage of glaciers, increasing desertification, spreading of tropical diseases, and setting of new records for high temperatures and for frequency of severe storms. All of these observations are consistent with the notion that our planet is warming.

The principal source of warmth on Earth is incoming radiation from the sun. To maintain a heat balance, heat is radiated from Earth back into space, largely as infrared radiation. Carbon dioxide is one of a number of gases, others including water vapor, methane, nitrous oxide, and chlorofluorocarbons, that trap infrared. Increasing atmospheric  $CO_2$  concentration acts to retain more heat, by reducing the amount of infrared energy radiated back to space [E]. Hence increasing  $CO_2$  links with increasing warming. While global temperatures and atmospheric  $CO_2$  concentrations appeared to have cycled up and down a long way back into Earth's history – long before humans even evolved – a profound piece of circumstantial evidence connected with the present



**Figure 1.6** The concentration of carbon dioxide in the atmosphere has been rising for many years. The present scientific consensus is that the steadily increasing use of fossil fuels worldwide is a major (but not the only) contribution to this increased  $CO_2$  concentration.

warming cycle is that the increase in atmospheric  $CO_2$  over the past several centuries began at about the same time as the Industrial Revolution, which marked the beginning of large-scale use of fossil fuels. It took millions of years to form fossil fuels. We have been burning them on a large, and ever-increasing, scale only for about 250 years. Thus the rate of  $CO_2$  addition to the atmosphere currently outstrips the rate of  $CO_2$  removal.

Buttressing this circumstantial evidence [F], recent years have seen further evidence added for a link between increased atmospheric carbon dioxide and human use of fossil fuels. Certainly, anthropogenic  $CO_2$  emissions from fossil fuel combustion are not the sole cause of global warming. Nevertheless, connections between global warming, atmospheric  $CO_2$ , and fossil fuel use confront us with several energy policy options. One, of course, is to do nothing. At the other end of the spectrum lies the argument that we must stop using fossil fuels *right now*.

History teaches us that some 60 to 70 years are needed for one fuel to replace another as the dominant energy source. In 1830, renewable fuels (mainly wood) dominated worldwide primary energy sources, accounting for more than 90% of total energy. Coal made up most of the rest. By 1900, the contribution from wood had dropped, and that of coal had increased, to a point at which both energy sources were accounting for nearly 50% of world energy use, with a very small contribution from petroleum. Coal dominated the world energy scene until 1965, when coal and petroleum each contributed about 30%, with natural gas and renewables about 15% each. Since 1965 petroleum has dominated the world energy scene. Perhaps at the end of another 70 year cycle, sometime around 2035, we will witness a resurgence of renewable energy sources, not just biomass, but also solar, wind, and other forms that do not involve combustion.

It is likely that we are now somewhere in the "transition state" between an energy economy heavily dominated by fossil fuels and a new one based on alternative energy sources. Plants, or fuels derived from plants, will contribute to the alternative energy mix. We need to understand the chemistry of these biofuels, but also to recognize that fossil fuels will be with us for decades to come, so we should be concerned with their conversion to clean, efficient fuel forms. Furthermore, we should recognize that, at the end of the transition, fossil fuels will be important sources of graphite, activated carbon, and other carbon-based materials.

## Notes

- [A] The recently discovered *Desulfatomaculum* bacteria provide an example. These remarkable organisms exist by reducing sulfate ions to hydrogen sulfide. They have flourished for several million years at depths to four kilometers in a gold mine near Johannesburg. Organisms able to manufacture their own compounds for use as energy sources are called autotrophs. By far the most familiar autotrophs are the green plants. Microorganisms living near deep-sea vents, where conditions are extremely hostile for ordinary life (such as 400°C, 25 MPa, and pH  $\approx$ 3), obtain energy by using heat from the vents for oxidizing inorganic sulfides or methane. Organisms that rely entirely on chemical reactions to manufacture their biochemical energy sources are chemoautotrophs. Especially weird are the radiotrophs, fungi found growing inside reactors at Chernobyl, Ukraine, that seem to utilize the energy in radiation to help synthesize needed biochemical energy sources. Organisms that must rely on eating other organisms to obtain a supply of energy are heterotrophs. We are heterotrophs.
- [B] Sooner or later, biology catches up to all of us. The expression "Mother Nature bats last," the origin of which has been attributed to numerous individuals, has appeared on bumper stickers for at least a decade. Or, as the American author Damon Runyon (1880–1946) said, "in life, it's 6 to 5 against," meaning the odds are against us.
- [C] We will not consider the decay process in detail, because it destroys the raw material (organic matter) needed eventually to produce coal, petroleum, and natural gas. For learning more about the decay process in nature, the book *Life in the Soil* (James B. Nardi, University of Chicago Press) is an excellent place to start.
- [D] Note that oxygen is a co-product. The first organisms using water as the source of electrons in photosynthesis the cyanobacteria evolved approximately three billion years ago. This development in the history of life allowed  $O_2$  to accumulate in the Earth's atmosphere. Chemically, this converted the atmosphere from a reducing environment to an oxidizing one, with profound implications for the further evolution of life.
- [E] While it is common to speak of the greenhouse gases acting to trap infrared radiation, they neither trap all of the radiation nor trap it permanently. Absorption of infrared by a greenhouse gas molecule excites the molecule to a higher vibrational energy state. Energy is released when the molecule returns to its ground state, but the energy is released in all directions, re-radiating a portion of it back to Earth.
- [F] Two of the finest minds of the nineteenth century provide contrasting opinions on the validity of circumstantial evidence. Henry David Thoreau tells us that, "Some circumstantial evidence is very strong, as when you find a trout in the milk." But Sherlock Holmes cautions that, "Circumstantial evidence is a very tricky thing. It may seem to point very straight to one thing, but if you shift your point of view a little, you may find it pointing in an equally uncompromising manner to something entirely different."

### **Recommended reading**

- Cuff, David J. and Goudie, Andrew S. *The Oxford Companion to Global Change*. Oxford University Press: New York, 2009. This is a very handy one-volume reference book with several hundred short articles, including useful material on the global carbon cycle, biomass and biofuels, and fossil fuels.
- McCarthy, Terence. *How on Earth?* Struik Nature: Cape Town, 2009. An introductory book on geology with superb color illustrations. Chapter 3, on the Earth's atmosphere and oceans, is relevant to the material in this chapter.
- Richardson, Steven M. and McSween, Harry Y. *Geochemistry: Pathways and Processes*. Prentice-Hall: Englewood Cliffs, NJ, 1989. A book on geochemical principles presented in the context of thermodynamics and kinetics. Chapter 4, on the oceans and atmosphere, and Chapter 6, on weathering of rocks, are useful for understanding the global carbon cycle.
- Schobert, Harold H. *Energy and Society*. Taylor and Francis: Washington, 2002. An introductory text surveying various energy technologies and their impacts on society and on the environment. Chapter 34 discusses the global carbon cycle and introduces the concept of biomass energy being a short-circuit in the cycle.
- Vernadsky, Vladimir I. *The Biosphere*. Copernicus: New York, 1998. This book was first published in 1926, and provides a remarkable discussion of how living organisms have transformed the planet, including the geochemical cycling of elements and the ways in which organisms utilize geochemical energy. The edition listed here is extensively annotated with explanations and findings through the 1990s.
- Williams, R.J.P. and Fraústo da Silva, J.J.R. *The Natural Selection of the Chemical Elements*. Clarendon Press: Oxford, 1996. This book presents aspects of the physical chemistry of distribution of chemical elements between living and non-living systems. Chapter 15 on element cycles includes a discussion of the global carbon cycle; other chapters also contain useful discussions of the partitioning of carbon between various natural systems.

## 2.1 Catalysis

The topic of catalysis recurs throughout fuel chemistry. A catalyst increases the rate of a chemical reaction without itself being permanently altered by the reaction, or appearing among the products. The key word is *rate*. Catalysts affect reaction kinetics. A catalyst affects reaction rate by providing a different mechanism for the reaction, usually one that has a markedly lower activation energy than that of the non-catalyzed reaction. Catalysts do not change reaction thermodynamics; they do not alter the position of equilibrium [A], but they can help reach equilibrium much more quickly. And, they cannot cause a thermodynamically unfavorable reaction to occur.

Catalysts can be classified as homogeneous, in the same phase as the reactants and products, and heterogeneous, in a separate phase. Homogeneous catalysts mix intimately with the reactants. This good mixing often leads to enormous rate enhancements, in some cases by more than eight orders of magnitude. But, because they are in the same phase as the reactants and products, industrial use would require a separation operation for catalyst recovery downstream of the reaction, unless one were willing to throw away the catalyst (possibly allowing it to contaminate the products) as it passes through the reactor. For many catalytic processes, the catalyst costs much more than the reactants do, so loss of the catalyst would result in a significant economic penalty. Usually, heterogeneous catalysts have no major separation problems, thanks to their being in a separate phase from reactants and products. However, because of their being in a separate phase, mass-transfer limitations can hold up access of the reactants to the catalyst, or hold up departure of products. Heterogeneous catalysis can also be affected by various problems at the catalyst surface (discussed in Chapter 13). Large-scale industrial processing almost always favors use of heterogeneous catalysts, to avoid possibly difficult downstream separation issues. Nevertheless, steady progress is being made in finding ways to overcome separation problems with homogeneous catalysts, including, as examples, membrane separation, selective crystallization, and use of supercritical solvents.

While, by definition, a catalyst remains unchanged at the end of a reaction, it can, and often does, change during a reaction. Mechanisms of many catalytic reactions often involve many steps, which collectively comprise the catalytic cycle. The catalyst might undergo change during one or more of the elementary reaction steps of the mechanism, but at the end, when its action is complete, the catalyst must emerge in its original form, ready for another catalytic cycle.

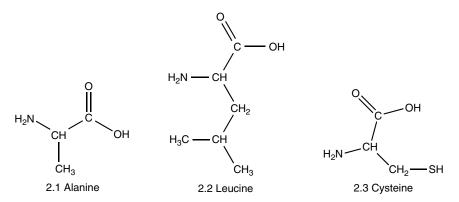
Most homogeneous catalytic reactions occur in the liquid phase. Some reactions can be catalyzed in the gas phase by homogeneous catalysts (which, because they are homogeneous, must be gases themselves). Probably the most important example of homogeneous catalysis in the gas phase is the chlorine-catalyzed decomposition of ozone, the reaction responsible for the so-called ozone hole in the atmosphere [B].

Various parameters can be used to describe quantitatively the quality or "goodness" of a catalyst. Turnover number, and the related turnover frequency, compare the efficiency of different catalysts. Turnover number indicates the number of molecules of reactant that one molecule of catalyst can convert into product. The term "turnover" comes from the notion that the catalytic conversion is "turning over" reactant molecules into product molecules. Turnover frequency is the turnover number expressed per unit time. Selectivity expresses the fraction of the desired product, usually in weight percent or mole percent, among all products of the reaction. Ideally, selectivity should be as close to 1, or 100%, as possible. Catalyst activity can be broadly defined in terms of rate of consumption of the reactant(s) or rate of formation of products. (These terms have slightly different meanings in the field of heterogeneous catalysis, and are revisited in Chapter 13.) Ideal catalysts are those with high selectivity and high activity.

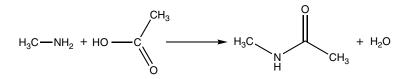
## 2.2 Proteins

Biochemical reactions in living organisms rely on homogeneous catalysts called enzymes. Enzymes provide superb activity and selectivity. Because most enzymes are proteins [C], we consider composition and structure of proteins first, leading into a discussion of enzymes and their catalytic behavior.

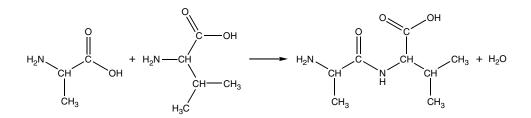
The building blocks of proteins are amino acids. These compounds contain both an amine and a carboxylic acid functional group. All naturally occurring amino acids of biochemical significance are 2-aminocarboxylic acids. Derivatives of carboxylic acids have sometimes been named using Greek letters to identify the positions on the carbon chain starting from the atom attached to the carboxylic group, with  $\alpha$ - indicating the carbon attached to the carboxylic acid,  $\beta$ - the next carbon in the chain, and so on. Hence 2-aminocarboxylic acids can be, and usually are, referred to as  $\alpha$ -amino acids. Twenty naturally occurring  $\alpha$ -amino acids are known, which differ in the nature of the organic substituent, generically called R, attached to the  $\alpha$ -carbon atom [D]. Alanine (2.1), leucine (2.2), and cysteine (2.3), provide examples.



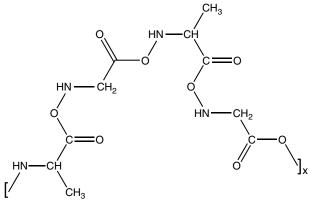
Amines can react with carboxylic acids to form amides, e.g. the reaction of methylamine with acetic acid:



Because amino acids contain both functional groups, one molecule of an amino acid can react with another to form an amide, e.g.



The two amino acids need not be identical, as shown in this example. With amino acids, the amide functional group is called a peptide linkage. The dipeptide produced in the reaction shown above still contains an amine and a carboxylic acid, thus can react with another amino acid molecule to produce tripeptides, and then tetra-, penta-... and up to very large, high molecular weight polypeptides. Polypeptides having molecular weights over 10 000 are called proteins. Fibroin (2.4), a constituent of natural silk, has perhaps the simplest protein structure.



2.4 Fibroin

Fibroin is a co-polymer of alanine and glycine, the two simplest amino acids. Proteins have numerous vital roles in living organisms. Certainly their role as enzyme catalysts is one of the most important.

Protein structure is considered at three levels. The number and kind of the individual amino acids in the protein, and the way that they are linked together, determines

the primary structure. Even small proteins are likely to contain more than 50 peptide linkages. The secondary structure of proteins arises from a very specific pattern of folding of the chain of amino acids into a helix or a pleated sheet. Secondary structure indicates how various segments of the protein molecule become oriented. Formation of secondary structure comes from an attempt to maximize the number of possible intramolecular hydrogen bonds between C=O and H-N groups. With large proteins, several secondary-structure helices might be joined together into a tertiary structure that could arise from intramolecular electrostatic interactions, further hydrogen bonding, or even formation of covalent bonds such as the disulfide linkage, - S-S -. The tertiary structure describes how the whole protein molecule acquires its threedimensional shape. Folding the protein into its tertiary structure occurs so as to involve the greatest possible loss of energy. Of all possible tertiary structures of a protein, the one that actually forms is the one having the lowest  $\Delta G$  of formation. Disruption of the secondary or tertiary structure of the proteins, such as by heating or a change in pH, destroys their physiological functioning, a process known as denaturation. Cooking egg whites provides a familiar example of denaturation; the antiseptic action of "alcohol" (i.e. isopropanol) on the skin comes from its ability to denature the proteins in bacteria.

Proteins are further classified, based on structure, as either fibrous or globular. Fibrous proteins have long, thread-like structures that often lie adjacent to each other to form fibers. Strong intermolecular forces facilitate this structural arrangement. Fibrous proteins are usually insoluble in water. They make the structural materials in organisms, including muscle, skin, and tendons. In contrast, globular proteins have roughly spherical structures that result from strong intramolecular forces, but have weak intermolecular forces. Globular proteins dissolve in water and in many aqueous solutions. Enzymes that are proteins are invariably globular proteins.

## 2.3 Enzymes

The excellent catalytic properties of enzymes derive from their molecular configuration, which provides a site at which, usually, only a single kind of molecule can enter and react. Enzymes are so specific that they catalyze reactions not just of one particular set of chemical bonds, but a set of bonds in a specific stereochemical configuration. Emil Fischer [E] (Figure 2.1) was probably the first scientist to use the analogy of a reactant fitting very specifically into the catalytic site on an enzyme in the way that a key fits into a lock.

In addition to great selectivity, many enzymes also demonstrate phenomenal activity, in exceptional cases enhancing reaction rates by 17 orders of magnitude. Of all the substances known to catalyze reactions, whether homogeneous or heterogeneous, enzymes are the most effective. Turnover frequencies can be of the order of  $10^3 \text{ s}^{-1}$ , exceptional in comparison with many heterogeneous catalysts, for which values might be in the range  $10^2-10^4 \text{ hr}^{-1}$ . The very great enhancement of reaction rates by enzymes means that they can have a noticeable effect even at very low concentrations, e.g.  $10^{-3}-10^{-4}$  mole percent.

The compound on which the enzyme acts as a catalyst is known as the substrate. The nomenclature of enzymes involves adding the suffix *–ase* to a word that indicates the function of the enzyme, or its substrate. As an example, the enzyme lactate dehydrogenase catalyzes the dehydrogenation (i.e. oxidation) of the lactate ion.

Type of enzyme catalyst	Reaction being catalyzed
Hydrolase	hydrolysis
Isomerase	isomerization
Ligase	linking two smaller molecules together
Lysase	removing a small segment of a larger molecule
Oxidoreductase	oxidation or reduction
Transferase	transfer of a structural group from one molecule to another

Table 2.1 Classes of enzyme catalyst.



Figure 2.1 Emil Fischer made enormous contributions to our understanding of protein chemistry and of sugar chemistry in the late nineteenth and early twentieth centuries.

Enzymes fall broadly into six classes, summarized in Table 2.1. Almost every known type of organic reaction has an enzyme-catalyzed counterpart.

During the reaction, the enzyme interacts with the substrate molecule(s), binding them to a specific location, the active site, in the enzyme molecule. Enzymatic reactions occur in three steps: formation of a complex between the substrate and the enzyme; converting the enzyme-substrate complex into an enzyme-intermediate complex, in which the configuration of the substrate molecule has changed; and finally formation of an enzyme–product complex, from which the product dissociates.

Interaction of enzyme with substrate could occur via hydrogen bonding, ionic attraction, or reversible covalent bonding. Whatever the interaction that occurs between the active site and the substrate, it is very specific for the substrate. Further, if the reaction is catalyzed by acid or by base, the active site must be capable of supplying the needed acidic or basic reactant. The secondary or tertiary structure of the enzyme strongly controls the orientation of the reactant molecules, such that they are stereochemically oriented for rapid reaction, and lead to a product having the biochemically correct stereochemical fit for the substrate – the lock has to be able to accept the key. The sketch in Figure 2.2 shows this. The complex formed between the enzyme and its substrate provides the optimum molecular orientation for reaction. Usually the product detaches immediately from the enzyme, making the enzyme available for



**Figure 2.2** The way in which one specific key fits into a lock provides a model for the very specific structural relationships between an enzyme and its substrate.

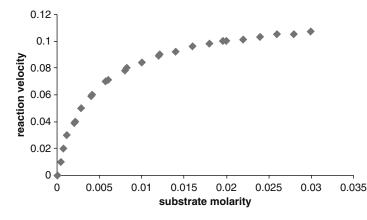
another reaction. A product tightly bound to the enzyme active site would effectively block that site from participating in further reactions, shutting down the catalytic activity of the enzyme. The turnover frequency is often  $10^3 \text{ s}^{-1}$  per reactive site in the enzyme; the best enzymes might reach  $10^5 \text{ s}^{-1}$ .

Just as a lock will only accept the correct key, enzymes are usually extremely specific in their action, such that any one particular biochemical reaction has its own corresponding particular enzyme catalyst. In some cases enzyme catalysis is so specific that only one compound will react with the enzyme. For example, urease catalyzes hydrolysis of urea, H<sub>2</sub>NCONH<sub>2</sub>, extremely well, yet has no effect for hydrolysis of methylurea, CH<sub>3</sub>NHCONH<sub>2</sub>. However, many enzymes can catalyze the reactions of substrates other than the desired one, provided that the changes in structure relative to the normal substrate occur in regions of the substrate molecule that do not affect the key-in-lock fit of substrate to active site. The catalytic activity of the enzyme might be reduced somewhat, but the reaction still proceeds. Situations occur in which a substrate binds strongly, often irreversibly, to the active site but does not undergo whatever reaction the enzyme catalyzes. Substrates of this kind make the enzyme unable to perform its normal catalytic function. Such substances are catalyst poisons; the analogous problem in heterogeneous catalysis is discussed in Chapter 13 [F].

Rates of enzymatic reactions can be expressed in several ways. The maximum velocity,  $V_{MAX}$ , represents the theoretical maximum rate when substrate concentration is high enough such that the active site in the enzyme would be constantly occupied by substrate. Maximum velocity is a specific property of a given enzyme, a function only of the amount of enzyme present in the system. The Michaelis constant [G],  $K_M$ , is the substrate concentration at which the measured rate of reaction is half the maximum velocity. Enzymatic reactions involving a single substrate follow Michaelis–Menten [H] kinetics, given by

$$v = V_{\text{MAX}}S/(K_M + S)$$

where v is the rate of reaction and S the concentration of the substrate. When v is plotted as a function of S, in the initial stages of reaction the rate increases rapidly as substrate concentration is increased, but, at some point, the rate becomes nearly constant and essentially independent of substrate concentration. Figure 2.3 illustrates Michaelis–Menten kinetics for a hypothetical enzymatic reaction. This behavior reflects, first, a situation in which there is more available enzyme than substrate, so that as substrate concentration increases, more and more of the enzyme can participate in catalysis; but, second, at some point all of the enzyme is engaged in the reaction and further increases in substrate concentration can have no effect.



**Figure 2.3** A Michaelis–Menten plot provides a simple model for the kinetics of an enzymatic reaction, relating reaction rate to substrate concentration. This curve is for a hypothetical reaction but is typical of the shape of this relationship.

Since the majority of enzymes are proteins, it is worth considering why some, but by no means all, protein molecules can act as catalysts (i.e. enzymes). In other words, why aren't all proteins enzymes? The answer lies in molecular structure, especially in the secondary and tertiary structure that sets up the appropriate spatial conformation of -C=O, -NH, or other groups that, collectively, provide a site capable of accommodating and binding a specific substrate molecule. The side chains on the individual amino acids may also be configured to create stronger intermolecular interactions with the desired substrate molecules. Stronger interactions between the substrate and the side chains of the amino acids in the enzyme could enhance bond-breaking reactions in the substrate. For some, not all, proteins, the secondary and tertiary structure is geometrically such that it forms the "lock" into which a specific biochemical "key" just fits. In the many proteins that do not serve as enzymes, the secondary and tertiary structure may not provide an appropriately configured binding site, or possibly cannot provide the acid or base needed to complete a reaction.

Because enzyme activity depends on secondary or tertiary structure, denaturation of an enzyme destroys its catalytic activity. In most cases, denaturation cannot be reversed. Exact conditions triggering denaturation are specific to each enzyme, but typically denaturation occurs about 10-15 °C above the temperature normally found in the cell. The temperature at which denaturation occurs can be reduced if major changes in pH happen at the same time.

In some enzymatic reactions, the enzyme must be activated by the addition, or presence, of a second substance, the cofactor. Some cofactors are inorganic ions, such as  $Fe^{+2}$  or  $Zn^{+2}$  [I]. Other cofactors are organic molecules, called coenzymes. During the catalytic process, the cofactor also attaches to the enzyme, and may experience either oxidation or reduction. For us, the most important of the coenzymes are the vitamins.

Interest in using enzymes in industrial processes is increasing. Reactions using enzymes are not limited to occurring in living organisms. Many enzymes have been isolated from organisms and are commercially available. They can be used to catalyze reactions in aqueous solution or sometimes in organic solvents. Enzymatic catalysis of reactions represents an important component of the emerging field of green chemistry, which includes among its goals using renewable raw materials, minimizing extra reagents or solvents, and designing processes with very low energy requirements. Green chemistry in turn is an important component of the broader field of sustainable development, which is intended to meet our present needs – certainly including energy, chemicals, and materials – without compromising society's ability to meet the needs of future generations.

#### Notes

- [A] Wilhelm Ostwald (1853–1932, Nobel Prize 1909), who almost single-handedly developed the field of physical chemistry, showed that this is a direct consequence of the First Law of thermodynamics. Consider a gas reaction that proceeds with a change in the number of moles of gas, and hence with a change in volume. Suppose that the reacting gases are confined within a cylinder fitted with a piston, and suppose further that the catalyst was in a small container in the cylinder, such that it could be alternately exposed to the reacting gases or shielded from them. If the catalyst could alter the equilibrium composition of the mixture, the piston would move up or down with the shift in equilibrium, creating a perpetual-motion machine.
- [B] The ozone "hole" is not, of course, a hole in the atmosphere, but the term describes a region of considerably diminished ozone concentration in the southern hemisphere, particularly over the Antarctic. Ozone in the stratosphere helps absorb incoming ultraviolet radiation from the sun. Exposure to high levels of ultraviolet radiation has been implicated as a cause of health problems such as skin cancer and cataracts. Chlorine atoms from the breakdown of chlorofluoro-carbon gases, released as aerosol propellants, or from refrigeration and air conditioning units, act as homogeneous catalysts to facilitate ozone decomposition. The 1995 Nobel Prize in chemistry was awarded to Paul Crutzen of the Netherlands and the American scientists Mario Molina and Sherwood Rowland for their work in understanding the formation and decomposition of ozone. This award came exactly one week after a prominent member of the United States Congress denounced the concept of the ozone hole as "pseudoscience."
- [C] While the great majority of enzymes are proteins, this is not true of all enzymes. A particularly important exception is the ribosomes, cell components that assemble proteins from amino acids.
- [D] In solution, the simple amino acids exist in a dipolar structure formed by transfer of a proton from the carboxyl group to the amino group, e.g. RCH(NH<sub>3</sub>)<sup>+</sup>COO<sup>-</sup>. This type of structure is known as a zwitterion. However, for convenience we use the formula RCH(NH<sub>2</sub>)COOH, which seems to be a long-standing convention in many organic chemistry textbooks.
- [E] Emil Fischer (1852–1919, Nobel Prize 1902) is probably best known for enormous contributions to understanding the structure and chemistry of sugars. He was also among the first to determine that proteins form from the reaction of amino acids. While the lock-and-key model remains an excellent way of thinking about enzymatic catalysis, it is not always correct. Daniel Koshland (1920–2007) showed in 1960 that some enzymes first accept the substrate molecule and *then* structurally rearrange to fit the substrate, the induced-fit model.

- [F] Many catalyst poisons harm both homogeneous and heterogeneous catalysts, because the basic effect is the same for either type of catalyst: the poison binds strongly to the active sites on the catalyst, blocking them from interacting with the desired reactant molecules. In fact, many catalyst poisons also poison *us*, examples being carbon monoxide and hydrogen sulfide. The underlying catalytic chemistry is exactly the same. These substances poison us because they destroy the activity of the enzymes on which our bodily functions depend.
- [G] Named in honor of Leonor Michaelis (1875–1949), a German biochemist whose career in the German scientific system was destroyed when, as a young man, he published work questioning the validity of a pregnancy test devised by a scientist very senior in the establishment. Michaelis first moved to Japan, and then to America, where he worked at Johns Hopkins University and at The Rockefeller Institute.
- [H] Maud Menten (1879–1960) was a Canadian biochemist who worked with Michaelis in Berlin. Also an excellent artist and musician, her contributions to science in addition to her work on enzyme kinetics included studies of hemoglobin and the regulation of blood sugar content. She also participated in several expeditions to the Arctic.
- [I] Many inorganic species serve as enzyme cofactors; other examples include copper and manganese. Inorganic ions that serve as cofactors are sometimes called essential minerals. Their presence in the diet is critical for good health, specifically because of their role as cofactors.

#### **Recommended reading**

- Faber, Kurt. *Biotransformations in Organic Chemistry*. Springer: Berlin, 2004; Chapter 1. The first chapter of this book provides a good overview of enzyme catalysis.
- Gates, Bruce C. *Catalytic Chemistry*. Wiley: New York, 1992; Chapter 3. A well-written book covering many of the fundamentals of catalysis and catalysts. Chapter 3 deals with enzymes.
- Grunwald, Peter. *Biocatalysis*. Imperial College Press: London, 2009. A very detailed treatment of enzymes and the mechanisms of enzyme-catalyzed reactions. Definitely a very useful book for those wanting to learn more about enzyme chemistry.
- McMurry, John. *Organic Chemistry*. Brooks/Cole: Pacific Grove, CA, 2000; Chapter 26. The discussion of proteins and enzymes in this chapter is intended to focus on the roles of enzyme catalysis in biosynthesis and in fermentation; i.e. to provide a background for the material in the next several chapters. Necessarily, an enormous amount of other information on enzymes and proteins was left out. A good place to start to explore further is in the relevant chapters in modern introductory texts on organic chemistry. Many good ones are available; this text by McMurry is a fine example.
- Palmer, Trevor and Bonner, Philip. *Enzymes*. Horwood Publishing: Chichester, UK, 2007. A comprehensive look at enzymes, including much useful information on their behavior and uses in both biochemistry and biotechnology.
- Rothenberg, Geri. *Catalysis: Concepts and Green Applications*. Wiley-VCH: Weinheim, Germany, 2008. An excellent introduction to catalysis, particularly as it applies to green chemistry and sustainable development. Chapters 3 and 5 are particularly relevant here.

# **3** Photosynthesis and the formation of polysaccharides

Photosynthesis is the single most important chemical process on Earth. Almost all life depends on photosynthesis, directly in the case of plants, or indirectly, in the case of animals that eat plants, or that eat other animals that in turn eat plants. In the geochemical history of Earth, the rise of green plants and their production of oxygen from photosynthesis converted the atmosphere from chemically reducing to oxygen-rich, making life as we know it able to evolve. As a carbon dioxide sink in the global carbon cycle, photosynthesis consumes about one hundred billion tonnes of carbon annually.

Photosynthesis converts atmospheric carbon dioxide to glucose:

$$6 \operatorname{CO}_2 + 6 \operatorname{H}_2 \operatorname{O} \rightarrow \operatorname{C}_6 \operatorname{H}_{12} \operatorname{O}_6 + 6 \operatorname{O}_2.$$

Few other chemical processes appear so simple when written as a single equation, but are so extremely intricate in detail [A]. The American chemist Melvin Calvin (Figure 3.1) received the 1961 Nobel Prize in chemistry for work in elucidating the reaction pathways in photosynthesis [B].

The remarkable nature of photosynthesis is further highlighted by the fact that the simple photosynthesis reaction, as written above, is quite strongly endergonic. The change in Gibbs energy,  $\Delta G$ , is +2720 kJ per mole of glucose (or +454 kJ/mol CO<sub>2</sub>) at 298 K. The corresponding equilibrium constant would be predicted to be far to the left-hand side. Photosynthesis can only proceed with the input of a significant amount



**Figure 3.1** Melvin Calvin, who made enormous contributions to understanding the chemistry of photosynthesis. Image courtesy of Lawrence Berkeley National Laboratory.

of energy from other sources. The non-spontaneous "photosynthetic engine" of life needs a supply of energy in order to function. This energy comes from the sun.

In photosynthesis, the carbon atom in carbon dioxide must undergo a formal reduction. Reduction processes require electrons. Driving the conversion of carbon dioxide to carbohydrates also requires energy. The reaction steps that, collectively, comprise the overall process of photosynthesis therefore must provide both electrons and energy. Carbohydrate metabolism in both plants and animals releases large amounts of energy, so necessarily the biosynthesis of carbohydrates requires an input of energy.

# 3.1 Water splitting in photosynthesis

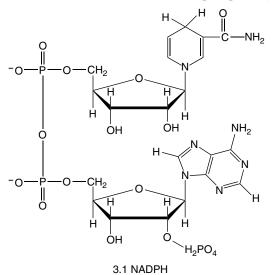
Before examining glucose formation, we first consider the co-product, oxygen. Both reactants contain oxygen atoms. The source of the  $O_2$  could be carbon dioxide, or water, or both. Determining the chemical source of the molecular oxygen represents one of the first applications of radioactive tracer techniques to investigate biochemical problems.

The radioactive isotope <sup>18</sup>O<sub>8</sub> is designated as O<sup>\*</sup> in the reactions below. Two reactions can be carried out:  $H_2O^* + CO_2$ , and  $H_2O + CO_2^*$ . Both can be run under photosynthetic conditions, and the products analyzed to determine the fate of the O<sup>\*</sup>. Radioactive O<sup>\*</sup><sub>2</sub> appears only in experiments that used radioactive water,  $H_2O^*$ , as a reactant; i.e. the oxygen derives entirely from water [C]. The equation for photosynthesis can be written as

$$6 \text{CO}_2 + 12 \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2 + 6 \text{H}_2\text{O},$$

to emphasize that twelve moles of water must be reacted (to account for the six moles of oxygen coming entirely from water). The six moles of water on the right-hand side of this equation must be products of another reaction [D].

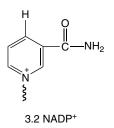
The electrons needed for the reduction of carbon dioxide derive from a coenzyme, nicotinamide adenine dinucleotide phosphate (3.1), NADPH [E].



This reaction can be written as

NADPH 
$$\rightarrow$$
 NADP<sup>+</sup> + 2e<sup>-</sup> + H<sup>+</sup>,

where NADP<sup>+</sup>, the oxidized form of NADPH, differs in having the structural unit shown as 3.2: (In this structure, the "squiggle bond" indicates a connection to the remainder of the molecule, which is identical with that shown previously for NADPH.) Regeneration of NADPH uses electrons derived from water:

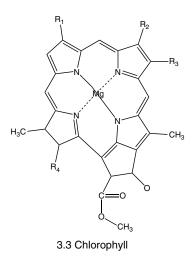


$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-,$$
  
 $2e^- + H^+ + NADP^+ \rightarrow NADPH$ 

so that

The important point about this process is the ultimate source of electrons for reduction of carbon dioxide, water.

The energy for the water splitting reaction derives from sunlight. Pigment molecules in the plant leaves absorb light. Chlorophyll (3.3) is the most important of these pigments.



Chlorophyll type	$R_1$	$R_2$	$R_3$	$R_4$
a	-CH=CH <sub>2</sub>	-CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>3</sub>	X*
b	$-CH=CH_2$	-CHO	-CH <sub>2</sub> CH <sub>3</sub>	X*
<i>c</i> <sub>1</sub>	$-CH=CH_2$	$-CH_3$	$-CH_2CH_3$	-CH=CHCOOH
<i>c</i> <sub>2</sub>	$-CH=CH_2$	$-CH_3$	$-CH=CH_2$	-СН=СНСООН
D	-CHO	$-CH_3$	$-CH_2CH_3$	X*

 Table 3.1 Structural differences between the varieties of chlorophyll.

\*The structure of X is a long chain,

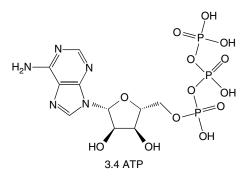
Five types of chlorophyll exist, differing in structural features as indicated in Table 3.1.

Of these, chlorophyll a is the most abundant. Chlorophyll absorbs energy from sunlight, promoting an electron from the ground state to an excited state:

 $Chl \to Chl^{\ast}.$ 

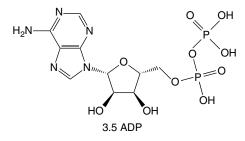
This step transforms solar energy to chemical energy. An electron in an excited state is more easily transferred than one in a ground state. Eventually electrons pass to NADP<sup>+</sup>, reducing it to NADPH, as shown above. NADPH participates in conversion of carbon dioxide to glucose.

This first major phase of photosynthesis involves conversion of radiant energy in sunlight into chemical energy in a group of compounds called "electron carriers" and into adenosine triphosphate (ATP), (3.4)



In the second phase, the electron carriers and ATP provide the chemical energy to drive the synthesis of glucose from  $CO_2$ .

ATP is a crucial component of all living cells for the capture, storage, and transfer of free energy from exergonic reactions to drive endergonic processes. In biochemical processes in living cells, ATP represents "energy currency" [1]. Synthesis of ATP from adenosine diphosphate (ADP) puts energy "in the bank," while energy can be "spent" by ATP when it transfers a phosphate group to another molecule and itself reverts to ADP, (3.5).

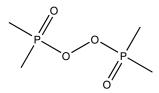


ATP hydrolyzes to ADP, releasing the hydrogen phosphate ion  $HPO_4^{-2}$  and releasing free energy. The conversions of ADP to ATP and back again to ADP are critical for energy use in living cells. This reaction can be represented as

$$ATP + H_2O \rightleftharpoons ADP + HPO_4^{-2} + free energy.$$

Usually the equilibrium lies far to the right, with about  $10^7$  times as much ADP as ATP. Driving the reaction to the left captures free energy and produces ATP.

ATP and the related ADP belong to the class of phosphoric acid anhydrides. The characteristic structure of these compounds looks like (3.6).



3.6 Phosphoric acid anhydride

This structure should appear quite similar to that of the more familiar carboxylic anhydrides, such as the useful reagent acetic anhydride. Carboxylic anhydrides readily react with alcohols to form carboxylic esters. For example, acetic acid reacts with ethanol:

 $CH_3COOCOCH_3 + CH_3CH_2OH \rightarrow CH_3CH_2OCOCH_3 + CH_3COOH.$ 

This reaction breaks a C–O bond in the anhydride. Phosphoric anhydrides react in analogous fashion. A P–O bond breaks, and a phosphate ester forms. Phosphate esters can be represented as  $ROPO_3^{-2}$ . If the phosphoric anhydride happens to be ATP, and the alcohol methanol, then the reaction proceeds as

$$ATP + CH_3OH \rightarrow ADP + CH_3OPO_3^{-2}$$

Chlorophyll in its excited state reacts to transfer its loosely held electron to an electron acceptor. Electron transfer in this fashion is a reduction reaction, in which Chl\* acts as the reducing agent. It triggers a biochemical oxidation–reduction process that could not have taken place in the dark, because light was required to promote an electron in chlorophyll. The reduction product can react further, by transferring electrons to other compounds of lower energy. The cascade of electron-transfer processes occurs only because each electron-carrier compound along the way has more energy than the compound to which the electron is transferred. Thus a release of energy occurs as the electron-transfer sequence proceeds.

Energy released from the cascade of electron transfer drives two separate, but related, processes. First, it results in synthesis of ATP. In this sequence of reactions, the electron originally lost from chlorophyll eventually gets back to the same chlorophyll molecule, giving a cyclic electron flow. Second, the energy release also results in synthesis of NADPH. This sequence of reactions oxidizes water:

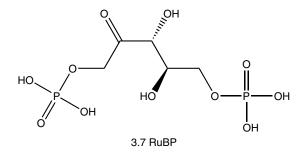
$$2 H_2 O \rightarrow O_2 + 4 H^+ + 4 e^-.$$

Electrons from oxidation of water replenish those lost from chlorophyll. This is the reaction that produces oxygen, consistent with the results of radioactive tracer experiments. Because the electron used to replenish the chlorophyll comes from water, this second sequence of reactions is called non-cyclic electron flow.

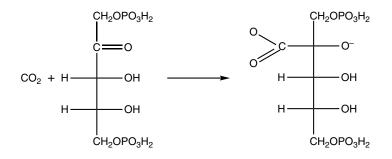
To summarize: Energy comes into the system as radiant energy in sunlight. This energy is absorbed by promoting Chl to Chl\*. Energy is then released during a sequence of electron flow reactions. ATP absorbs and stores the released energy. Non-cyclic electron flow reactions account for splitting of the reactant water molecules.

# 3.2 Carbon dioxide fixation

"Fixation" or "fixing" [F] of carbon dioxide occurs via reaction with a molecule of ribulose-1,5-bisphosphate (RuBP), (3.7).

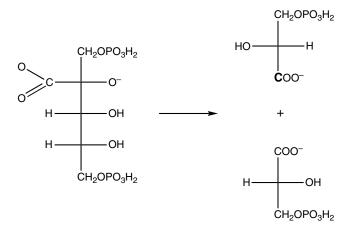


The reaction involves enzyme-catalyzed interaction of CO<sub>2</sub> with the carbonyl carbon atom in RuBP:

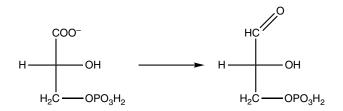


(The structures shown above, and in many of the reactions to come, are called Fischer projections, in which, for simplicity, the carbon atoms at the "crosses" are customarily not shown. The name for this type of structural representation honors the great organic chemist Emil Fischer (Figure 2.1) [G].) The enzyme catalyzing this reaction, RuBP carboxylase (also known as RUBISCO), has two distinctions. First,

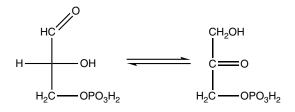
its size,  $\approx 480000$  Da, makes it one of the largest enzyme molecules. Second, RUBISCO can account for up to 30% of the total proteins in leaves; this makes RUBISCO the most abundant protein in the world. The relatively unstable product of carbon dioxide fixation promptly decomposes into two molecules of 3-phosphoglycerate:



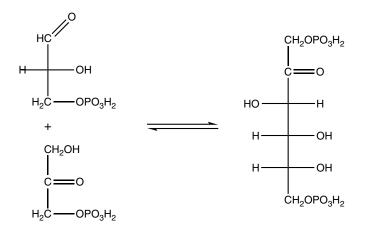
The two molecules from this reaction are identical; one has been drawn inverted relative to the other to illustrate how the reactant splits in the middle to give the two 3-phosphoglycerate molecules. The carbon atom introduced by fixation of carbon dioxide is indicated in larger, bold font. 3-Phosphoglycerate then converts to glyceraldehyde-3-phosphate. Conversion of a carboxyl group to an aldehyde is a reduction, in which NADPH serves as the reducing agent.



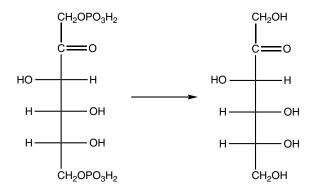
Glyceraldehyde-3-phosphate has great importance not only in photosynthesis, but also in reaction pathways that are discussed in Chapters 4 and 5. In photosynthesis, glyceraldehyde-3-phosphate isomerizes to dihydroxyacetone phosphate:



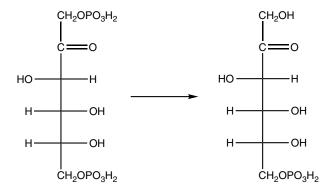
Dihydroxyacetone phosphate reacts with glyceraldehyde-3-phosphate to form fructose 1,6-diphosphate:



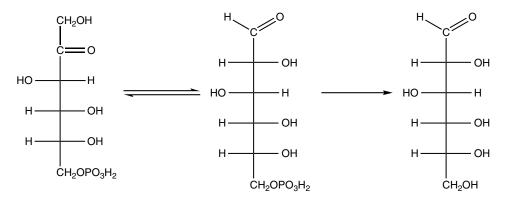
Loss of the phosphate groups from fructose 1,6-diphosphate produces fructose. Shuttling of phosphate groups is handled by ATP and ADP.



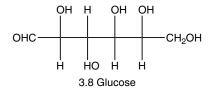
Fructose occurs in a variety of fruits, which gives rise to its common name, fruit sugar; it is also the dominant sugar in honey. Loss of a single phosphate group produces fructose 6-phosphate:



This compound isomerizes to glucose 6-phosphate:



from which the loss of phosphate leaves glucose (3.8).

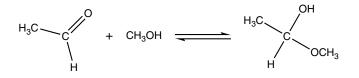


# 3.3 Glucose, cellulose, and starch

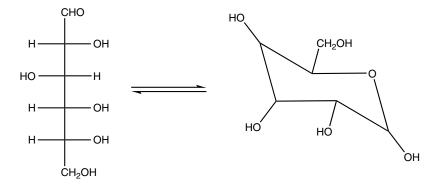
Sugars, as well as starch and cellulose discussed later in this chapter, belong to the broad family of carbohydrates. A useful classification of sugars employs a three-part name: a prefix *keto-* or *aldo-* that indicates whether the carbonyl group is a ketone or aldehyde, a second prefix indicating the number of carbon atoms in the molecule (usually but not always *pent-* or *hex-*), and the suffix *-ose*, which indicates that the molecule is a sugar. In this classification scheme fructose is a ketohexose, glucose an aldohexose.

Of all the many sugars produced by living plants, by far the most important is glucose. Glucose contains four asymmetric carbon atoms, so that there exist 16 (i.e.  $2^4$ ) isomeric aldohexoses, eight pairs of optically active enantiomers [H]. Glucose is the one aldohexose of the 16 with special importance in fuel chemistry.

The Fischer projection implies that glucose has a linear structure. In fact, glucose, as well as many other pentoses and hexoses, exists in equilibrium with a cyclic structure. The cyclic structure results from a characteristic reaction of aldehydes with alcohols. This reaction can be illustrated by considering, for simplicity, acetaldehyde and methanol:



Reaction of an aldehyde with an alcohol produces hemiacetals. Glucose is an aldehyde, but also richly endowed with alcohol functional groups. Therefore glucose can form an intramolecular hemiacetal, as do other hexoses and pentoses. Whenever there is potential for forming a five- or six-membered ring via intramolecular reactions, it is good to be alert to the possibility that such cyclizations might actually occur. In living cells, pentoses and hexoses do not exist in the linear configuration implied by the Fischer projection, but rather as cyclic intramolecular hemiacetals, e.g.



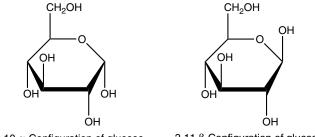
In cells or in solution the equilibrium in this reaction lies far to the right.

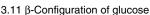
The cyclic forms of these compounds have their own special nomenclature. Pyranoses, with a six-membered ring having five carbon atoms and one oxygen atom, as shown above for glucose, derive their name from the simple heterocyclic compound pyran (3.9).



3.9 Pyran

The name of the cyclic structure of glucose, glucopyranose, indicates that it is the cyclic, pyran-like, structure of glucose. When the ring closes in the formation of the hemiacetal, another carbon atom in the molecule - the former carbonyl carbon becomes chiral, i.e. has four different groups attached to it. When this happens, a new pair of diastereoisomers is formed, called anomers. By extension, the carbon atom participating in hemiacetal formation is called the anomeric carbon. Two configurations of the anomeric carbon,  $\alpha$  (3.10) and  $\beta$  (3.11) can be formed, easy to discriminate if the cyclic hemiacetal structure is considered to be flat, a structural representation known as the Haworth projection [I].

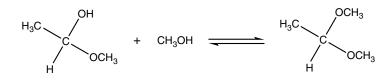




In these structures, the –OH on the anomeric carbon atom can be thought of as being "down" relative to the plane of the ring, or *trans*- across the ring from the –CH<sub>2</sub>OH group in the  $\alpha$ -anomer, and as being "up" relative to the ring, or *cis*- relative to –CH<sub>2</sub>OH in the  $\beta$ -anomer. Glucose is dextrorotatory (i.e. rotates plane-polarized light to the right), or a "D" sugar, so the full name of the hemiacetal form would be  $\alpha$ -D-glucopyranose, or  $\beta$ -D-glucopyranose. In aqueous solution, glucopyranose exists in a 36:64 mixture of the  $\alpha$  and  $\beta$  forms. Five-membered ring structures, with four carbon and one oxygen atom, are called furanoses, from the parent compound furan (3.12):

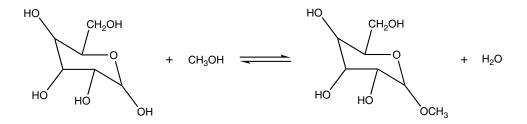


Hemiacetals have, among their characteristic reactions, the possibility of reacting with another molecule of alcohol, producing an acetal. Using the hemiacetal of acetaldehyde and methanol as an example:



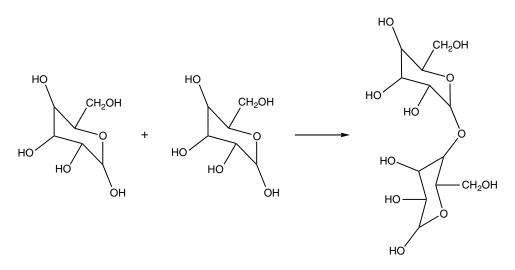
Acetals can be thought of as being a special class of diethers, ones in which both ether linkages are attached to the same carbon atom. Many acetals undergo hydrolysis fairly easily, whereas most common ethers, such as diethyl ether, do not. This property of acetals is revisited in Chapters 4 and 8. Acetal formation can also be considered as being a reaction of two moles of alcohol with a carbonyl group. An analogous reaction also proceeds with ketones, the products being ketals. Of particular importance is the fact that the two steps in acetal or ketal formation, e.g. aldehyde  $\rightarrow$  hemiacetal  $\rightarrow$  acetal, are both easily reversible. The reaction can be driven in either direction; in many systems, equilibrium normally favors the free carbonyl compound.

The hemiacetal form of sugars participates in acetal formation. Glucose can also form an acetal with methanol:



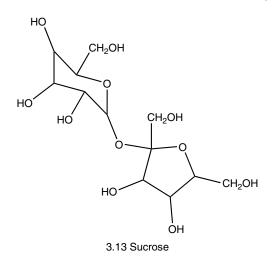
Acetals of carbohydrates such as glucose are called glycosides. The products of this reaction are methyl  $\alpha$ -D-glucopyranoside, in about 65% yield, and methyl  $\beta$ -D-glucopyranoside, accounting for about 35%.

Sugar molecules, with alcohol groups, form an acetal between the hemiacetal group in one sugar molecule and an –OH group on another molecule, e.g.

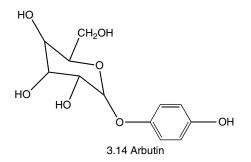


The new ether bond resulting from formation of an acetal at the hemiacetal site in a sugar is called a glycoside linkage. Two monosaccharides join via a glycoside linkage to form a disaccharide. In principle, any of the –OH groups on one sugar molecule can react at the anomeric hemiacetal carbon of the other molecule. Of particular importance is the glycoside linkage between the anomeric  $C_1$  carbon and the  $C_4$  –OH of the other sugar molecule, as illustrated above. These specific glycoside linkages are called 1,4' links. The glycosidic bond at the anomeric carbon can be of  $\alpha$  or  $\beta$  configuration, i.e. a 1,4'- $\alpha$  glycoside.

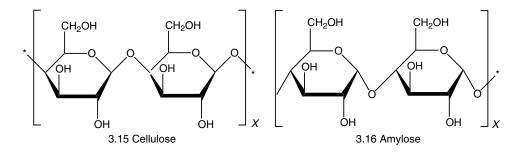
The example shown above uses identical monosaccharide molecules. It is not necessary that this be the case; for example, glucose and fructose form the very common disaccharide sucrose, also known as table sugar (3.13), a 1,2'-glycoside



Further, a large family of naturally occurring glycosides exists in which only one component is a monosaccharide. For example, the natural compound arbutin (3.14), [J] is a glycoside of glucose and hydroquinone:



Formation of a disaccharide produces a molecule that still possesses an available hemiacetal site and plenty of --OH groups. A disaccharide could react further to make a trisaccharide, and then tetra-, penta-... and on to very high molecular weight polysaccharides. Two polysaccharides based on glucose are of great importance, cellulose (3.15) and starch (3.16).



Cellulose and starch are very nearly, but not quite, identical. Both polysaccharides consist entirely of the monosaccharide glucose and have the same elemental compositions. Only one major difference exists, which may be a seemingly small or trivial one, but which has enormous ramifications. The difference lies in the stereochemical configuration of the glycoside linkage between the glucose units. The structural difference between cellulose and starch provides an example of the critical importance of stereochemistry. Humans have glycosidase enzymes that easily hydrolyze the acetal linkage in starch, but cannot cleave the one in cellulose. Thus we can (and do!) digest starchy foods like potatoes, but cannot digest wood. In addition to the impact on human agriculture and nutrition, our ability to metabolize starch and not cellulose becomes important in the development of a biofuels industry. This point is revisited in Chapter 4.

Plants synthesize cellulose as a structural component, to add strength and rigidity to the plant. Cellulose, the most abundant organic compound on Earth, is a polymer of thousands of individual glucose units, all linked by  $1,4'-\beta$ -glycoside bonds. The strength and rigidity derive in part from the ability of cellulose chains to form hydrogen bonds with adjacent chains. A group of cellulose molecules so arranged forms a microfibril, usually several micrometers long and the core of which is perfectly crystalline. A typical cellulose molecule might contain about 8000 individual glucose units.

Plants synthesize starches for energy storage when, later, a source of biochemical energy is needed. Starch is somewhat more complicated structurally. Structure 3.16 represents amylose, a component of starch in which the linkages are  $1,4'-\alpha$ -glycosides. Amylose molecules contain about a thousand glucose units. Amylose has a helical structure, the helix having six glucose units in each turn. Amylopectin also consists of glucose units linked by  $1,4'-\alpha$ -glycosides, but in addition, contains some  $1,6'-\alpha$ -glycoside linkages, which serve to create branch points, giving amylopectin a branched structure. Amylopectin can contain up to 50000 glucose units. The relative proportions of amylase and amylopectin in plant starches vary from one species to another; for example, potato starch is about 80% amylopectin.

#### Notes

- [A] Actually, another was also introduced in Chapter 1, the seemingly simple combustion of methane,  $CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$ . The mechanism of the complete combustion of methane might involve several hundred elementary reaction steps.
- [B] Apparently the Nobel Prize committee did not consult with Calvin's high school physics teacher, who told Calvin that he would never be a successful scientist because he was too impulsive. Despite having to take time out to work in a brass factory in Detroit for financial reasons, Calvin became the first person to receive a chemistry degree from Michigan Tech (1931). His Ph.D. was from Minnesota (1935). During the oil shortages of the 1970s, Calvin became very interested in exploiting the sap from plants of the genus *Euphorbia* as a source of biofuels. The gopher plant (*Euphorbia lathyrus*) and the milk bush (*Euphorbia tirucalli*) produce sap that is an emulsion of petroleum-like hydrocarbons in water. Separation and work-up of the organic component of these saps produces liquid hydrocarbons. Unfortunately, the best yields would be about 10 cubic meters of liquid per hectare, meaning that it would require some  $2.4 \times 10^5$  hectares to supply the *daily* refinery input in the United States alone.
- [C] This finding also involves a stroke of luck, in that quite possibly  $O_2^*$  could have come from both  $CO_2^*$  and  $H_2O^*$ , and/or that  $O^*$  could have appeared in both the  $O_2$  and the glucose. Either or both of these outcomes would have made unraveling the chemistry of photosynthesis all the more complex.
- [D] This process happens with the transfer of hydrogen from NADPH to 3-phosphoglycerate:  $(C_3H_5O_4)PO_3H_2 + 2$  NADPH  $\rightarrow (C_3H_7O_4)PO_3H_2 + 2$  NADP. The product decomposes to glyceraldehyde 3-phosphate:  $(C_3H_7O_4)PO_3H_2 \rightarrow (C_3H_5O_3)PO_3H_2 +$  $H_2O$ . The reaction occurs to six molecules of 3-phosphoglycerate, forming six molecules of water.
- [E] Phosphorus has virtually no role in fuel chemistry. But, it should be clear from the central role of ATP in plant biochemistry that phosphorus plays a vital role in plant growth. This can be verified easily by inspecting the label on a bag of lawn and garden fertilizer. One of the important measures of the quality of a fertilizer is its phosphorus content.
- [F] The term "fixation" refers to depriving a substance of its volatility, i.e. converting a gas or easily vaporized liquid into a solid or non-volatile liquid form. This usage

derives from the alchemists at least as far back as the end of the fourteenth century. The term may have been coined by the alchemist John Gower, who was a contemporary of Chaucer, and who may have influenced the discussion of alchemy in Chaucer's *The Canon's Yeoman's Tale* from *The Canterbury Tales*.

- [G] Emil Fischer (1852–1919, Nobel Prize 1902) enjoyed an illustrious career in organic chemistry. While best known for his research on sugars, he contributed greatly to the chemistry of proteins (see note [E] to Chapter 2), purines, caffeine, and dyes. Fischer was allowed to attend university studies in science by his father, a very successful businessman, who judged young Emil too stupid to go into business.
- [H] Optical activity and the topic of stereochemistry in general have little role in fuel chemistry, although this situation could change as emphasis on the biofuels and the biological (e.g. enzymatic) processing of fuels increases in years to come. There are numerous fine introductory textbooks on organic chemistry, including those by Jones and by McMurry mentioned below; invariably they have at least one chapter devoted to optical activity and stereochemistry.
- [I] Norman Haworth (1883–1950, Nobel Prize 1937) originally intended to go into business with his father, designing and manufacturing linoleum. His interest in the dyes used in this business led to a broader interest in organic chemistry and ultimately to the Nobel Prize. In addition to his notable researches in sugar chemistry, his other accomplishments included one of the first syntheses of ascorbic acid (vitamin C), which led to inexpensive commercial production of this important compound.
- [J] Arbutin occurs naturally in cranberries and blueberries. It sometimes finds medical use as a diuretic. The glycosides are a large family of compounds of which many have interesting, useful, or dangerous properties. The cardiac glycosides, e.g. digitonin, help to stimulate contractions of the heart muscles. The cyanogenic glycosides contain a nitrile group; when these compounds are hydrolyzed, they release hydrogen cyanide, HCN. Many plants can utilize HCN with no adverse effects, but it can kill us.

#### Reference

[1] McMurry, J. Organic Chemistry. Brooks/Cole: Belmont, CA, 2004; p. 1096.

#### **Recommended reading**

- Abeles, Robert H., Frey, Perry A., and Jencks, William P. *Biochemistry*. Jones and Bartlett: Boston, 1992. Chapter 23 discusses the biochemistry of photosynthesis.
- Goodwin, T.W. and Mercer, E.I. *Introduction to Plant Biochemistry*. Pergamon Press: Oxford, 1983. Chapter 5 presents the biochemistry of photosynthesis in very great detail. A very useful source for readers wishing to go beyond the level of information presented here.
- Jones, Maitland. Organic Chemistry. Norton: New York, 1997. Chapter 24 of this excellent introductory text on organic chemistry discusses carbohydrates, and has a particularly detailed discussion of Fischer's heroic determination of the structure of glucose.
- Kramer, Paul J. and Kozlowski, Theodore T. *Physiology of Woody Plants*. Academic Press: Orlando, 1979. Chapter 5 discusses, among other things, how environmental factors, such as light intensity, shading, and temperature, affect photosynthesis.
- Mauseth, James D. *Botany*. Jones and Bartlett: Boston, 1998. Chapter 10 discusses photosynthesis, with information on how and where the process occurs in cellular structures within plants.

34

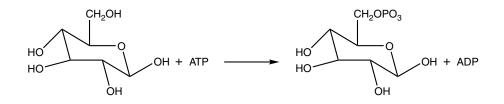
- McMurry, John. *Organic Chemistry*. Brooks/Cole: Pacific Grove, CA, 2000. Another excellent introductory text on organic chemistry, with useful additional information on stereochemistry, optical isomerism, and carbohydrate chemistry.
- Morton, Oliver. *Eating the Sun*. HarperCollins: New York, 2008. Subtitled "how plants power the planet," this book is devoted to explaining photosynthesis at an introductory level. A good introduction to the topic.
- Purves, William K., Sadava, David, Orians, Gordon H., and Heller, H. Craig. *Life: The Science of Biology*. Sinauer Associates: Sunderland, MA, 2001. Chapter 8 of this text provides a good discussion of photosynthesis.
- Smil, Vaclav. *Energy in Nature and Society*. MIT Press: Cambridge, MA, 2008. Chapter 3 discusses photosynthesis largely from the perspective of energy production and energy flows.

# 4.1 Fermentation chemistry

Fermentation represents the first or second chemical process to be exploited deliberately by humankind. The other contender is combustion, i.e. controlled use of fire. Fermentation of sugars, particularly glucose, produces ethanol. Ethanol was probably the first organic chemical to be produced on a large scale. Ethanol's importance in fuel chemistry lies in its use as a liquid transportation fuel, either blended with, or as a replacement for, gasoline.

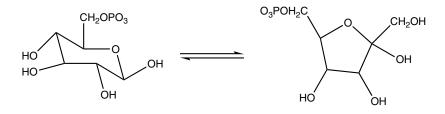
Fermentation begins with enzyme-catalyzed hydrolysis of a polysaccharide to glucose. Starches tend to be easier to hydrolyze than cellulose. Consequently, starches are, at present, the preferred feedstock for ethanol production. As mentioned in Chapter 3, humans can digest starches but not cellulose. Therefore, the possible diversion of large quantities of starch into ethanol production has significant ramifications, which are discussed later in this chapter.

Glucose becomes phosphorylated by enzyme-catalyzed reaction with ATP, producing  $\alpha$ -glucose-6-phosphate:

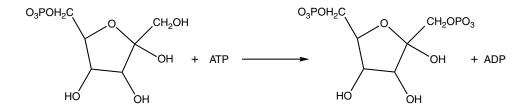


In many biochemical processes a thermodynamically unfavorable reaction can proceed by combining it with at least one additional reaction that is favored, provided that the net change in  $\Delta G$  for the two (or more) combined reactions is negative. The reaction of glucose with HOPO<sub>3</sub><sup>-2</sup> is not, by itself, favorable. But the reaction of glucose with ATP to form  $\alpha$ -glucose 6-phosphate and ADP has a net  $\Delta G$  that is negative. The utility, and great importance, of ATP in biochemical processes stems from its ability to drive reactions that would otherwise be unfavorable, such as the phosphorylation of glucose.

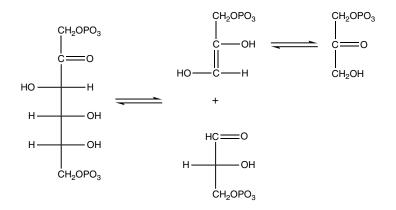
 $\alpha$ -Glucose 6-phosphate isomerizes to fructose 6-phosphate, converting an aldohexose to a ketohexose. Isomerization relies on keto-enol tautomerism; the exact reverse of this isomerization was presented in Chapter 3. Isomerization of  $\alpha$ -glucose 6-phosphate to fructose 6-phosphate proceeds as



A second phosphorylation, catalyzed by phosphofructokinase, converts fructose 6-phosphate to the 1,6-bisphosphate, again via reaction with ATP:

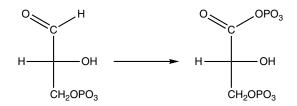


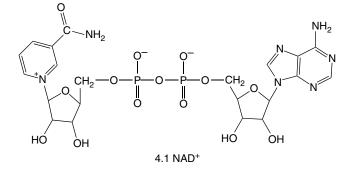
Fructose 1,6-bisphosphate splits into two molecules of glyceraldehyde-3-phosphate, one of which isomerizes into dihydroxyacetone phosphate. Thus:



These reactions should be familiar from Chapter 3; here they proceed in reverse. Dihydroxyacetone phosphate isomerizes, via enzyme-catalyzed keto-enol tautomerism, to another molecule of glyceraldehyde 3-phosphate.

Glyceraldehyde-3-phosphate is oxidized from aldehyde to acid form and phosphorylated to produce 1,3-bisphosphoglycerate:



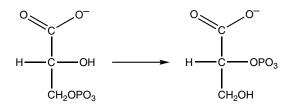


This step involves the coenzyme nicotinamide adenine dinucleotide NAD<sup>+</sup> (4.1),

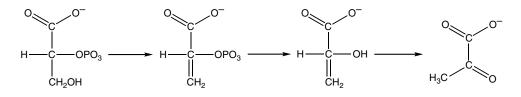
and the  $HOPO_3^{-2}$  ion [A]. NAD<sup>+</sup> serves as an electron carrier in biochemical systems; NAD<sup>+</sup> is an oxidizing agent, i.e. an electron acceptor, the corresponding reducing agent being NADH, which donates electrons. 1,3-Bisphosphoglycerate transfers a phosphate to ADP, regenerating ATP,



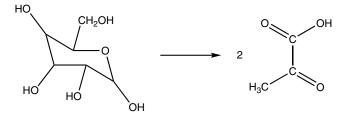
and forming 3-phosphoglycerate, which isomerizes to 2-phosphoglycerate:



2-Phosphoglycerate is converted to the important intermediate pyruvate (or, in its protonated form, pyruvic acid):



In sum, the overall process to this point converts a glucose molecule to two molecules of pyruvate (or pyruvic acid):

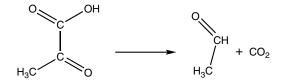


Conversion of glucose into pyruvate is called glycolysis; the reaction sequence is the Embden–Meyerhoff pathway [B]. In terms of chemical composition, it converts one molecule of  $C_6H_{12}O_6$  to two molecules of  $C_3H_4O_3$ . Since the total product is hydrogen-deficient relative to the starting material, this conversion must be an oxidation reaction, e.g.

$$C_6H_{12}O_6 + 2[O] \rightarrow 2C_3H_4O_3 + 2H_2O_3$$

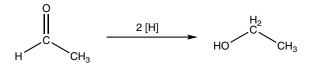
The sequence of sugar synthesis discussed in Chapter 3 depended on electron-transfer (reduction) reactions, so it is reasonable to expect that the chemical decomposition of sugar molecules depends on oxidation chemistry.

Once pyruvate, or pyruvic acid, has been formed, several things can happen, depending on the reaction conditions and the biochemistry of the specific organism [C]. Enzymes catalyze conversion of pyruvic acid to ethanol, particularly those enzymes occurring in yeast. Yeasts are unicellular fungi. Yeasts having an important role in fermentation belong to the species *Saccharomyces*, fermenting just about any material containing simple saccharides [D]. In the first step, pyruvic acid decarboxylates to acetaldehyde:



Pyruvic acid, having two functional groups, carboxyl and carbonyl (ketone), on adjacent carbon atoms, is the simplest member of the family of compounds called  $\alpha$ -keto acids.  $\alpha$ -Keto acids readily decarboxylate in the manner shown for pyruvic acid, forming carbon dioxide and an aldehyde containing one fewer carbon atom than in the parent acid.

Finally, acetaldehyde is reduced to ethanol:



# 4.2 Commercial production of ethanol via fermentation

Several routes exist for production of ethanol on a commercial scale. An alternative to fermentation chemistry is hydration of ethylene,

$$CH_2 = CH_2 + H_2O \rightarrow CH_3 - CH_2OH.$$

This reaction requires moderately severe conditions, e.g.  $250 \,^{\circ}$ C, and an acidic catalyst such as phosphoric acid. Worldwide, ethylene hydration accounts for about four billion liters (about three million tonnes) of ethanol production annually, primarily for industrial rather than beverage use. However, virtually all of the world's ethylene comes from processes using petroleum or natural gas as its source. In the context of energy policies that focus on reducing petroleum imports, reducing use of fossil fuels, or preparing for a future decline in petroleum production, the ethylene route is a "non-starter" [E].

The alternative involves industrial-scale fermentation of biomass. Many feedstocks can be used. These divide into two categories, the first in which the sugars are present in polysaccharides, such as starch or cellulose; and the second, in which the sugars are present as simple mono- or disaccharides, such as molasses or sugar cane. Blackstrap molasses, the unpurified liquid processed in the sugar cane industry, from which no more sugar can be crystallized, still contains 55% free sugar. Evaporating the untreated juice from sugar cane produces a material of 70–80% sugar, called high-test molasses. Biomass feedstocks in the first category require a preliminary grinding or milling operation to break down the plant cell walls and expose the starch to a hydrolysis medium. This preliminary operation adds to the capital expense and operating cost for an ethanol production facility.

In the United States, corn starch provides the feedstock for ethanol production. Two processing strategies are used, wet milling and dry milling. The differences lie in the preparation of the corn for subsequent treatment, principally whether the corn is milled or ground dry, or in the presence of water. Wet milling provides four useful by-products: corn steep liquor, a useful source of nitrogen; corn oil; corn gluten meal, a high-protein animal feed; and corn gluten feed, a lower-value, but still useful, animal feed. Also, if the carbon dioxide were captured from the fermentation step, it too could be a marketable byproduct. In contrast, dry milling provides only a single byproduct, distillers' dried grains with solubles, a valuable livestock feed (though again carbon dioxide could be captured for sale as well). Dry milling is becoming the favored process, largely because of its lower capital cost, and hence lower start-up costs for those entering the ethanol business.

Figure 4.1 presents a block flow diagram for conversion of starch to free glucose. The grain is pulverized and suspended in water. It is then degerminated: floating seeds and other plant debris are removed by skimming. Drying and then mechanically pressing the material recovered from degermination yields corn oil and a press cake that is used as cattle feed.

Heating the "mash" with steam liberates sugars by hydrolysis. Hydrolysis is further enhanced by enzyme catalysis, the enzymes being added with malt [F]. The heat and enzymes together effect the hydrolysis of starch to monosaccharides.

The resulting solution proceeds to a fermentation reactor. Enzymes from yeasts catalyze the fermentation reactions [G]. Fermentation occurs typically at about 27-32 °C and a pH of 3–5, with a residence time of 48–72 hours, as a batch process. The overall reaction can be written as

$$C_6H_{12}O_6 \rightarrow 2 CH_3CH_2OH + 2 CO_2.$$

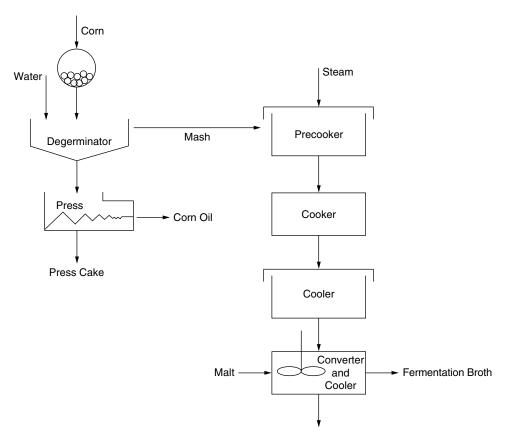
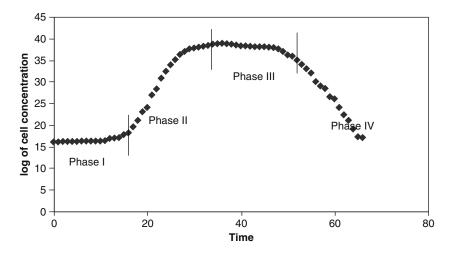


Figure 4.1 Process flow for liberation of starch from corn, and subsequent hydrolysis of the starch to glucose.

It is exothermic, with  $\Delta$ H at standard conditions being –68.9 kJ/mol of glucose. Yield of ethanol can be 90–95% on a mass basis; the ratio of heats of combustion of the ethanol produced relative to glucose consumed is about 98%. (From a different perspective, the yeast gets very little energy benefit from converting glucose to ethanol.)

Fermentation proceeds to a concentration of 8-12% ethanol. The reaction stops because of the cumulative effect of several factors that destroy the yeast, including elevated temperature, ethanol concentration, and pH (which drops because of the formation of by-product organic acids). The reactors can be of enormous size, sometimes  $10^6$  liter capacity. The concentration of cells in the reactor changes as a function of time as shown in Figure 4.2.

The axes in Figure 4.2 are not scaled, since it represents a generic case of a batch bioreactor, and is not intended to portray any specific process. Four distinct phases can be seen in the curve. In phase I, the lag phase, the cells are becoming acclimatized to the system and getting ready to begin their biochemical work. Phase II, exponential growth, represents the period where the growth rate of new cells is proportional to the cell concentration. In Phase III, the stationary phase, the growth rate is zero because of one or more limitations, e.g. the lack of necessary nutrients. The decrease in cell concentration in Phase IV, the death phase, results from build-up of toxic



**Figure 4.2** The four phases of cell growth in a bacterial reactor, illustrated with arbitrary time and concentration units for a typical reaction. Phase I is the lag phase, Phase II exponential growth, Phase III the stationary phase, and Phase IV the final phase or "death" phase.

reaction products. This particularly applies to fermentation, because ethanol concentration eventually reaches a point of being lethal to the yeast cells.

For a reaction system in which one of the products inhibits the growth of cells, the rate constant can be found from

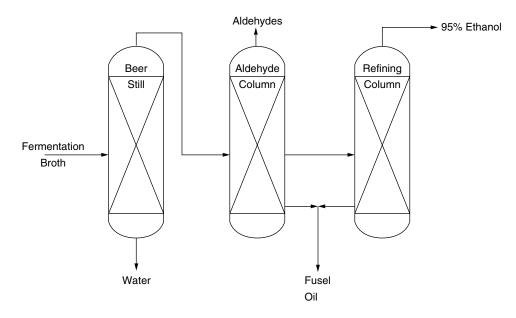
$$k = (1 - C_{\rm p}/C_{\rm p}^{*})^{n}$$

where the empirical constant *n* is 0.5 for glucose fermentation to ethanol, and  $C_p^*$ , the product concentration at which metabolism ends, is 93 g/dm<sup>3</sup> [1].

The effluent from the fermenter is called fermentation broth, or beer. To produce fuel-grade ethanol, the beer is subjected to a sequence of distillations, see Figure 4.3.

The first distillation produces, as overhead, a material that is about 55% ethanol. This product, sometimes called high wine [H], passes to a second column, which produces 95% ethanol. Ethanol forms a 95:5 azeotrope with water, so simple distillation of the fermentation broth can proceed only to this concentration of ethanol. (An azeotrope is a mixture of two or more liquids that has a constant boiling point; i.e. its composition cannot be changed by distillation.) Some of the by-products of fermentation – especially aldehydes; acetic, lactic, and succinic acids; and other alcohols – are removed in the second column [I]. The mixture of alcohols includes propanol, 2-methyl-1-propanol (isobutyl alcohol), 2-methyl-1-butanol (sometimes called primary active amyl alcohol), and 3-methyl-1-butanol (isoamyl alcohol). The distillation bottoms, called fusel oil, is described as "an oily liquid with disagreeable odor" [2]. Final production of 100% ethanol, called absolute ethanol or anhydrous ethanol, requires "breaking" the 95:5 ethanol:water azeotrope in a third distillation. This can be done by adding a third component, such as benzene or cyclohexane, to create a ternary azeotrope. As one example, addition of benzene to 95% ethanol produces a water-ethanol-benzene azeotrope that can be distilled off, leaving behind the anhydrous ethanol.

A significant challenge in fuel engineering, which could have a dramatic impact on the energy balance for ethanol production, is to find ways of replacing the



**Figure 4.3** Process flow for the distillation operations involved in obtaining 95% ethanol from fermentation broth.

energy-intensive distillation operations with another separation process, or processes, that would require much less energy. The multiple distillation steps represent a significant investment of energy, which reduces the net energy balance, i.e. the ratio of energy obtained in ethanol to that used in its manufacture. Separation technology that could provide high yields of anhydrous ethanol with fewer distillation steps would be a boon to ethanol production. One such technology is molecular sieving using synthetic zeolites. Zeolites comprise a large family of naturally occurring crystalline aluminosilicate minerals that have characteristic pore structures. They are discussed in Chapter 14 in conjunction with their use as heterogeneous catalysts. The virtue of synthetic zeolites lies in the ability to tailor pore size during the synthesis process, to achieve a desired separation of molecules based on size or shape. Final dehydration of 95% ethanol makes use of synthetic zeolites with pores of about 0.3 nm diameter. At this size, water molecules, about 0.44 nm, can not. Membranes with selective permeability for one of the two components could also offer a low-energy route to ethanol separation.

From Figure 4.1, if an ethanol production process were to use a starting material that already consisted of mono-saccharides and disaccharides, it would be possible to simplify the "front end" considerably. Potential feedstocks could be blackstrap or high-test molasses.

## 4.3 Ethanol as a motor vehicle fuel

In recent years, and from time to time in the past [J], ethanol has been recommended as a replacement for gasoline, or as a material to blend with gasoline. Blending could be done either to extend available supplies of gasoline or to improve gasoline properties. In

	Ethanol	Gasoline
Density, g/cm <sup>3</sup> at 20 °C	0.789	0.69–0.80
Atmospheric boiling point, °C	78.5	27-225
Latent heat of vaporization, MJ/l at 20 °C	0.662	0.251
Flash point, °C	12.8	-43 to -39
Autoignition point, °C	423	495
Flammability limits, volume percent in air	4.3–19	1.4-76
Lower heating value, MJ/l at 20 °C	21.09	32.16
Stoichiometric air/fuel volume ratio	14.32	55
Water solubility, weight percent at 20 °C	infinite	0.009
Research octane number	111	88-98
Vapor pressure, kPa at 38 °C	16	42–103

Table 4.1 Comparison of selected properties of pure ethanol (E100) and gasoline [4].

the first scenario, either anhydrous ethanol or the 95:5 ethanol:water azeotrope could be considered for use. When ethanol is blended with gasoline, a symbol such as E10 describes the blend; E signals that the blend contains ethanol, and the number indicates the percentage of ethanol in the blend. Continuing this example, E10 indicates a blend of 10% ethanol in gasoline. Pure ethanol would be E100.

Gasoline has immense importance as a motor vehicle fuel. Annual world consumption amounts to about  $1.2 \times 10^9$  m<sup>3</sup> [3]. Chapters 12 and 14 discuss the production and important properties of gasoline. Necessarily, this chapter refers to some of these properties, but without the detailed explanations that appear later. Table 4.1 compares some of the important properties of E100 and gasoline.

The octane number of a fuel indicates how well the fuel resists knocking, i.e. detonation of a portion of the unburned fuel–air mixture outside the flame front typical of normal combustion (discussed further in Chapter 14). The octane number of ethanol is about 111, substantially higher than most commercial grades of gasoline for vehicles, which range from 87 to 94. Ethanol can be used as a fuel in high-compression-ratio engines, which provide the advantage of having a greater thermal efficiency, i.e. of converting more of the chemical energy in the fuel–air mixture into mechanical energy in the engine. A particular application is in race cars; the Indy Racing League, which sponsors the annual Indianapolis 500 race in the United States, uses ethanol as fuel. Alternatively, ethanol can be blended with gasoline as an octane-booster for low-octane gasolines.

Oxygenated compounds have lower heats of combustion than those of the corresponding hydrocarbon molecules. The energy available from burning a gasoline/alcohol blend is less than that from an equivalent volume of gasoline. This difference adversely affects the fuel economy of the vehicle. Otherwise, performance of gasoline–alcohol blends is good. Table 4.2 summarizes effects of ethanol addition on knock-limited compression ratio and thermal efficiency. The knock-limited compression ratio is determined in a laboratory engine that has a variable compression ratio; with a specific fuel being tested, the compression ratio is increased until the point of incipient detonation is determined.

For most vehicles, the volume of the fuel tanks, not the mass of the fuel, limits the amount of fuel that can be carried. For practical use, volumetric energy density, i.e.

Percent ethanol in blend	Knock-limited compression ratio	Thermal efficiency
0	6	0.32
10	6.2	0.33
25	8	0.36
50	10	0.38
100	>10	0.38

 Table 4.2 Effects of blending ethanol into gasoline on knock-limited compression ratio and thermal efficiency [5].

the heat of combustion per unit volume, provides more information on vehicle range between refueling stops than does energy density per unit mass. Ethanol has about 66% of the volumetric energy density of gasoline (Table 4.1). A driver would get about two-thirds of the fuel economy (i.e. liters per kilometer or miles per gallon) with ethanol relative to gasoline, assuming comparable vehicles and driving conditions.

Volumetric energy density has two components, heat of combustion per unit mass and density. Comparing ethanol with gasoline, the factor accounting for most of the difference is the heat of combustion. The origin of the difference can be illustrated by comparing two reasonably similar molecules, propane and ethanol. Both have a "backbone" of three atoms, and their molecular weights are comparable, 44 vs. 46 Da, respectively, yet their enthalpies of combustion are remarkably different, -2043 kJ/ mol for propane vs. -1235 kJ/mol for ethanol. Conceptually, ethanol might be thought to be derived from propane by replacing a  $-CH_2$ - group in the propane structure with an -O-. The significant decrease in enthalpy of combustion results because ethanol is already partially oxidized compared to propane, and the partial oxidation itself is exothermic. The enthalpy of reaction for the process

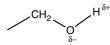
$$CH_3CH_2CH_3 + 2O_2 \rightarrow CH_3CH_2OH + CO_2 + H_2O$$

is about -808 kJ/mol for each mole of ethanol produced. The enthalpy of this reaction does not contribute to the enthalpy of combustion of ethanol; it is already gone, no longer available to us [K].

Pure ethanol has a much lower vapor pressure than gasoline. (Because vapor pressure depends on temperature, of course any meaningful quantitative comparison of vapor pressures must be made using data taken at the same temperature.) Continued comparison of ethanol with propane helps shed light on why this is the case. If the only factor affecting the vapor pressure were the kinetic energy needed for a molecule to escape the liquid into the vapor phase, it might be reasonable to expect that the boiling temperatures of these compounds would differ by only a few degrees, because of their similar molecular masses. In reality, the difference is  $120 \,^{\circ}$ C,  $-42^{\circ}$  for propane vs.  $78^{\circ}$  for ethanol.

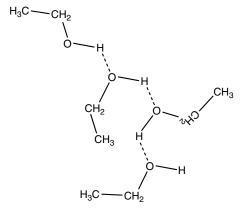
Propane has no permanent dipole moment. The carbon and hydrogen atoms have nearly identical electronegativities (2.5 vs. 2.1 on the Pauling scale), so that electrons in the C–C and C–H bonds are shared nearly equally between the atoms. The only forces that keep propane in the liquid phase are weak, temporarily-induced dipoles, van der Waals or London forces (Chapter 9). It takes only a little energy, typically about 0.1-5 kJ/mol, to disrupt these forces and "kick" a propane molecule from the

liquid to the vapor phase. In contrast, a significant difference in electronegativity between oxygen and hydrogen (3.5 vs. 2.1) leads to polarization of the bond (4.2).



4.2 Polarization of OH bond in alcohols

Bond polarization gives ethanol a permanent dipole moment, leading to significant electrostatic interactions between ethanol molecules. In ethanol, and many other molecules containing polarized bonds of hydrogen to oxygen, nitrogen, or fluorine, intermolecular interactions occur via hydrogen bonds (represented by dashed lines in structure 4.3).



4.3 Hydrogen bonding among ethanol molecules

Hydrogen bond interactions are much stronger than van der Waals interactions among hydrocarbons, but not so strong as covalent bonds. Hydrogen bonds typically represent energies of 4-50 kJ/mol, whereas covalent bonds are in the order of hundreds of kilojoules per mole. The additional energy needed to disrupt the hydrogen bonding is responsible for the substantially increased boiling point of ethanol relative to propane [L].

Reid vapor pressure (RVP), commonly used to express the vapor pressure of gasoline and related fuels, is the pressure inside a closed vessel held at 38 °C with a 4:1 ratio of volume of vapor to volume of liquid. The RVP of a typical gasoline can be about 70 kPa, whereas that of ethanol is about 16 kPa. Vapor pressure relates to two issues of engine or vehicle performance. On hot summer days, a very volatile (i.e. high vapor pressure) fuel can evaporate in the fuel line before reaching the engine. This evaporation sets off a cascade of problems, starting with an upset in operation of the fuel pump, leading to loss of pressure to the fuel injectors, and then to engine stalling, the condition being called a vapor lock. Such cases make it difficult to restart the engine until it has cooled enough to allow the fuel to condense back to the liquid state. In cold winter weather, a fuel must be volatile enough so that at least some vaporizes when injected into the cylinder, allowing the engine to "fire" even at low temperatures. For this cold start performance, a fuel of high vapor pressure is desirable. It would be reasonable to expect that a vehicle operating on ethanol would experience fewer vaporlock problems but worse cold-start performance than a comparable vehicle using gasoline. An ironic turn of events is consideration of blending gasoline back into ethanol to improve cold-start behavior.

For ethanol–gasoline blends, adding ethanol raises the vapor pressure. This may seem counterintuitive, but occurs because ethanol forms azeotropes with many components of gasoline. Thanks particularly to hydrogen bonding, ethanol–ethanol intermolecular interactions are stronger than interactions of ethanol with any of the hydrocarbon molecules. Consequently, gasoline–ethanol blends give good cold-start performance, but potentially can suffer from vapor-lock problems.

In gasoline-fueled engines, three undesirable products of combustion are carbon monoxide, a mixture of nitrogen oxides lumped under the formula NOx, and a mixture of unreacted or partially reacted fuel molecules called unburned hydrocarbons. Without effective controls on exhaust emissions, such as a catalytic converter, these so-called tailpipe emissions can be emitted to the atmosphere. In the presence of sunlight, they interact to produce the air pollution problem known as photochemical smog, usually just called "smog." Emissions of CO, NOx, and unburned hydrocarbons are lower from ethanol-fueled engines. The oxygen atom in the ethanol molecule shifts the combustion stoichiometry. For example, the complete combustion of octane, used here to represent gasoline,

$$C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O_3$$

requires 1.56 moles O<sub>2</sub> per C atom. Complete combustion of ethanol,

$$\mathrm{C_2H_5OH}\,+\,3\,\mathrm{O_2}\rightarrow2\,\mathrm{CO_2}\,+\,3\,\mathrm{H_2O},$$

requires 1.50 moles  $O_2$  per C atom. In the terminology of engine combustion, ethanol would be said to burn leaner, i.e. at a higher air-to-fuel ratio than gasoline. Leaner burning helps reduce CO emissions by favoring more complete combustion of the fuel. It also helps reduce  $NO_X$  emissions because the flame temperature is lower. The higher latent heat of vaporization of ethanol relative to gasoline (Table 4.1) gives a cooler flame and less  $NO_X$ . The lower vapor pressure of ethanol means fewer evaporative losses and lower unburned hydrocarbon emissions.

Gasoline and water don't mix, the solubility of gasoline in water being about 0.009% (Table 4.1). If gasoline becomes contaminated with water, a layer of water – the "water bottom" – will form at the bottom of storage tanks, fuel tanks at service stations, and vehicle fuel tanks. It may be possible to salvage much or all of the gasoline by a simple, physical phase-separation process. In contrast, ethanol and water are infinitely miscible. If an ethanol–gasoline blend is placed in contact with a water bottom, ethanol will diffuse into the water. This can cause a number of problems, including: reduction of octane number of the blend; loss of ethanol from the fuel system, along with any beneficial properties it might have provided; and contamination or pollution of the water by ethanol or other dissolved organic compounds. Pure ethanol fuels, E95 or E100, can potentially be diluted enough to have serious adverse effects on fuel properties. Therefore, attention must be paid to keeping ethanol, or ethanol blend, systems as water-free as possible.

In the early days of the Brazilian ethanol program, ethanol caused corrosion of fuel system and engine parts. This no longer seems to be a problem and has been addressed by appropriate materials selection. Because of its much different molecular polarity and hydrogen-bonding capability, ethanol can soften, swell, or possibly even dissolve polymers that are unaffected by hydrocarbons. This is of concern for seals in the engine and fuel system. In the gasohol (E10) program in the United States during the 1970s, some car manufacturers announced that warranties would be void if the owner used gasohol. This problem also can be alleviated by appropriate selection of materials.

On storage, some gasolines can form gums, high-molecular weight, insoluble materials of ill-defined structure. Gum formation occurs via oligomerization of alkenes and alkadienes, by reaction at their double bonds. Gums can clog fuel filters or fuel injectors. The absence of alkenes or alkadienes from ethanol means that gum formation is not a problem with ethanol fuels. Gum formation from ethanol–gasoline blends is reduced by reducing the alkene concentration via dilution.

Operation at low temperatures, other than the cold-start issue, is not a problem for ethanol. Neither viscosity nor outright freezing is a problem. Ethanol freezes at -117 °C; clearly there is no danger of its freezing at any realistic driving temperature.

## 4.4 Issues affecting possible large-scale production of fuel ethanol

Several crucial issues still need to be resolved for development, and acceptance, of a large ethanol fuel program in any nation. These include the energy balance,  $CO_2$  neutrality, available land and water resources, and the food vs. fuel debate.

The issue of energy balance centers around whether more energy is required to produce ethanol in the first place than is liberated when the ethanol is used as a fuel. In Brazil, where ethanol is made from sugar cane, the ratio of the energy obtained in the ethanol to the energy used in its production is  $\approx 3.7$ . The comparable figure for the United States, where the feedstock is corn starch, has been hotly debated. Best estimates suggest a ratio of  $\approx 1.5$  (compared with approximately 20 for petroleum). In other words, the energy produced when burning ethanol as a fuel does not exceed by much the energy that was consumed to make it. Some analysts have argued that the ratio of output to input energy is actually <1.

In Brazil, all of the necessary process heat for ethanol production comes from burning bagasse, the waste material left after crushing the cane to extract the sugarladen juice. In the United States, process heat is supplied by burning natural gas. In a sense, the energy used in Brazilian ethanol production is free. A further advantage of the use of bagasse is that its burning does not contribute to an increase in atmospheric carbon dioxide, on the presumption that any  $CO_2$  from bagasse combustion would be removed from the atmosphere within a few months by photosynthesis during the growth of the next crop. The name, *sugar* cane, also indicates an advantage for Brazilian practice. Sugar cane is about 20% sugar, the carbohydrates present as mono-saccharides and disaccharides. With sugar cane feedstock, the energy input needed for hydrolysis of starch (as in using corn as feedstock) is eliminated. Sugar cane is fairly easy to grow with relatively simple agricultural methods. Under particularly favorable conditions, two crops can be harvested per year, though one per year is common. In contrast, corn requires many more energy-intensive operations such as plowing, tilling, and fertilizing.

A major factor in the interest in biomass fuels is the desire to reduce substantially, or ideally eliminate, a net increase in  $CO_2$  concentration in the atmosphere. In principle,

biomass fuels should be  $CO_2$  neutral, in the sense that any  $CO_2$  produced during their production and subsequent combustion would be absorbed from the atmosphere within a year as the next crop of biomass is grown. For sugar cane ethanol,  $CO_2$  neutrality may be able to be realized, in part because of the use of bagasse for process heat. With corn starch as a feedstock, additional  $CO_2$  emissions include those from agricultural machinery such as tractors, from fertilizer manufacture, and from using natural gas as the process fuel.

The land and water resources needed for growing the necessary biomass, be it sugar cane, corn, or some other feedstock, cannot be neglected. For an energy economy in which ethanol, e.g. E100, would displace gasoline, it is abundantly clear that there is not enough arable land in the United States to produce the necessary corn. Many crops that are current or potential feedstocks for biofuels have large requirements for water. Whether fresh water or recycled water supplies would be adequate to sustain a massive world-wide energy economy based on biofuels is uncertain.

A significant problem with using corn for ethanol production lies in the fact that we eat corn, and even more so we eat animals that were raised on corn. Diverting large amounts of corn from human or animal food to fuel production raises a moral and ethical question, especially given the levels of malnutrition and hunger in the world today. Are we justified in using an excellent food crop to make fuel? (This question, often known as the "food vs. fuel" debate, applies as well to other potential food crops, not just corn.) The debate itself is outside the realm of science and engineering, but bears heavily on science and engineering practice. On one hand, a significant increase in the price of corn would directly impact animal feed (and, consequently, the prices of chicken, beef, and pork) as well as human food. In turn, this price increase would have a serious impact, particularly on persons of low income. On the other hand, at least in the United States, much of the price of packaged foods actually comes from the costs of processing, packaging, and distribution to stores. The cost of the actual food ingredients themselves represents only a fraction – sometimes a small one – of the total cost of the item. It can also be argued that price increases for corn help invigorate depressed or stagnant rural economies.

## 4.5 Cellulosic ethanol

Starch serves as a feedstock for making ethanol because it can be conveniently hydrolyzed to glucose, which in turn can be fermented to ethanol. But cellulose too is a polymer of glucose. Humans lack the enzyme for hydrolyzing cellulose. Using cellulose as a feedstock for ethanol production means that human foodstuffs are not being diverted into fuel production. It would be even more advantageous if the plants grown as a source of cellulose did not require prime agricultural land for their growth, nor intensive fertilization and cultivation practices. The term cellulosic ethanol applies to ethanol produced using cellulose as the feedstock. There is no chemical difference between this ethanol and ethanol from any other source; the adjective merely signals the source of the ethanol.

In many plants, cellulose is combined in the cell walls with a related material, hemicellulose, and a rather different biopolymer, lignin; the combination of these substances is called lignocellulose. Hemicellulose and lignin are treated in more detail in Chapter 6. Processing challenges lie in finding effective and efficient ways to separate the lignocellulose from the remainder of the plant material, then to separate the cellulose and hemicellulose from the lignin, to find facile chemical or enzymatic processes for hydrolyzing the cellulose and hemicellulose, and to use lignin as an energy source (analogous to bagasse) or possibly to convert it into useful chemical products. In addition, cellulose has endured through eons of plant evolution, to become the most abundant organic compound on Earth, because of its beneficial effects of protecting plants against the ravages of bacteria and fungi, as well as attack by weather. The resistance of cellulose to chemical and biochemical degradation, which serves so well in the living plant, makes it difficult to degrade cellulose when we want to hydrolyze it for ethanol production. Many enzymes react only slowly. Chemical attack can involve rather fearsome reagents such as concentrated aqueous sodium hydroxide, or hot concentrated sulfuric acid.

Switchgrass (*Panicum virgatum*) may become a feedstock of choice for cellulosic ethanol production. If grown in large-scale farming operations year after year, some of the same concerns will emerge as already seen with corn: the reliance on a monoculture crop, soil erosion, water consumption, and requirements for pesticides and herbicides.

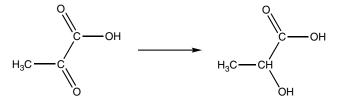
Production of cellulosic ethanol begins with one or more size-reduction operations to reduce the particle size of the feedstock. Then, a pretreatment step "loosens" the cellulose molecules, separating them from lignin and removing the hemicellulose by hydrothermolysis, i.e. reaction in hot water. Once the cellulose molecules have been made available for attack, saccharification converts cellulose into glucose and xylose, facilitated by cellulolytic enzymes. Fermentation of the resulting sugar solution could be done by yeasts, as used in conversion of starch to ethanol. However, the enzymes in yeasts do not ferment pentoses. To obtain a maximum ethanol yield, future cellulosic ethanol production processes could utilize genetically modified microorganisms having the capability of fermenting both pentoses and hexoses. Finally, the aqueous ethanol solution must be distilled. The lignin-rich solids not converted in this process could be used as a fuel for generating process heat.

There is ample room for improvement in cellulosic ethanol, from selection of feedstocks through cellulose separation and hydrolysis. Nevertheless, a consensus seems to be emerging that starch-based ethanol, especially made from corn, is only a stopgap source of ethanol until economic and efficient cellulosic ethanol processes are developed.

#### Notes

- [A] NAD<sup>+</sup> and its reduced form, nicotinamide adenine dinucleotide (NADH), are closely related structurally to the NADPH introduced in Chapter 2, the latter having one additional phosphate group. NAD<sup>+</sup> is a useful biochemical oxidizing agent.
- [B] The name honors the German biochemists Gustav Embden (1874–1933) and Otto Meyerhoff (1884–1951, Nobel Prize 1922). Before turning to carbohydrate metabolism, Embden studied metabolic processes in the liver, contributing to early understanding of diabetes. Meyerhoff was a co-recipient of the 1922 Nobel Prize in medicine for studies of metabolism in muscle tissue. Meyerhoff was Jewish, but fortunately avoided being caught up in the Holocaust, and arrived in Philadelphia in 1940, where he spent much of the rest of his life.

[C] In the absence of oxygen in the human body, pyruvic acid is reduced to lactic acid:



This condition sometimes occurs when we are using energy from glucose or starch so fast that we cannot supply enough oxygen to oxidize pyruvate to  $CO_2$ . Lactic acid accumulates in the muscles and gives rise to the "burn" experienced when exercising or working hard. When muscles begin to "burn," this is an indication that we have tipped from aerobic to anaerobic conditions inside our bodies.

- [D] In very rare cases, humans can be afflicted with colonies of the yeast *Candida albicans*. In the intestinal tract, these yeast colonies ferment just about any source of sugar, such as in candy, pastries, or beverages. A person whose intestinal tract contains this yeast can innocently ingest a sugar-containing food or beverage and become completely drunk, for no apparent reason. The unlucky person essentially serves as a human fermentation vat. Fortunately, nowadays antibiotics can destroy these yeast colonies.
- [E] Dehydration of ethanol to produce ethylene is relatively easy. In principle, ethanol derived from fermentation of natural materials could be dehydrated to serve as a renewable source of ethylene and, by extension, ethylene-derived materials such as polymers.
- [F] Malt is the product of the process of "malting" grains, such as barley. In this process, the grain is allowed to sprout, usually by soaking it in water, but further germination is stopped by drying the sprouted grain in hot air, e.g. in a kiln. The malting process helps produce enzymes that facilitate the breakdown of starch to sugar.
- [G] Yeasts are unicellular fungi, of which some 1500 species are known. Of special importance here is the *Saccharomyces cerevisiae* yeast, responsible for fermentation in the production of ethanol. The name *Saccharomyces* translates loosely as "sugar fungus." An exciting new development in applications of yeast in energy technology is their role in microbial fuel cells, which use microorganisms to convert chemical to electrical energy.
- [H] Beer and wine are limited to 15%, by volume, of ethanol. Obtaining higher concentrations of ethanol, to produce such beverages as rum, vodka, or whiskey, requires at least one distillation step. Alcoholic beverages of this type are referred to as "distilled spirits." Strictly speaking, a spirit contains no added sugar or flavorings, whereas distilled alcoholic beverages to which sugar and/or flavorings have been added are called liqueurs. The word "spirit" in this application probably derives from alchemy; when alchemists heated an object and a vapor was given off, that vapor was said to be the "spirit" of whatever substance was being heated. For example, ammonium carbonate, having the trivial name hartshorn, decomposes to ammonia and carbon dioxide on heating; the solution produced by capturing the ammonia in water used to be called "spirits of hartshorn."
- [I] The characteristic and distinctive flavors of varieties of alcoholic beverages, such as wines and whiskeys, derive from small quantities of fermentation by-products, such

as isoamyl alcohol and its acetate ester, ethyl butanoate and hexanoate, and 2-phenylethanol.

- [J] There is a long history of interest in ethanol as a motor vehicle fuel, going back probably to the late nineteenth century. In 1917 Henry Ford met with President Wilson to try to persuade him that America should move to an ethanol-based vehicle fleet. History would have been very different! During the 1920s and 30s, many countries had sizeable fuel programs involving ethanol blends with gasoline, including countries in Europe and South America. In the midwestern United States, Agrol Fluid, a blend of 78% ethanol, 15% benzene, and 7% of other alcohols, was a modest success, accounting at one time for 75 million liters of annual sales.
- [K] Of course the enthalpy for the hypothetical conversion of propane to ethanol is not truly "gone," as can be seen from the fact that the enthalpy of combustion of propane (-2043 kJ/mol) is the sum of the enthalpies of oxidation of propane to ethanol (-808 kJ/mol) and of combustion of the ethanol (-1235 kJ/mol).
- [L] The all-time champion in this regard is water, which is capable of forming two intermolecular hydrogen bonds with neighboring molecules. Water has a molecular weight of 18 Da and a boiling temperature of 100 °C. The comparable values for the related hydrocarbon molecule, methane, are 16 Da and -162 °C. Despite a molecular weight difference of only 2 Da, the difference in boiling temperatures is 262 °C.

#### References

- Fogler, H.S. *Elements of Chemical Reaction Engineering*. Pearson Education International: Saddle River, NJ, 2006; p. 424.
- [2] Budavari, S. The Merck Index. Merck and Co.: Rahway, NJ, 1989; p. 676.
- [3] Statistics from the International Energy Agency website, http://www.iea.org.
- [4] Adapted from extensive data in Klass, Donald L. Biomass for Renewable Energy, Fuels, and Chemicals. Academic Press: San Diego, 1998; p. 392.
- [5] Schobert, H.H. The Chemistry of Hydrocarbon Fuels. Butterworths: London, 1990; p. 314.

#### **Recommended reading**

- Brannt, W.T. Distillation and Rectification of Alcohol. Lindsay Publications: Bradley, IL, 2004; and Wright, F.B. Distillation of Alcohol and De-Naturing. Lindsay Publications: Bradley, IL, 1994. These two books are inexpensive paperback reprints of monographs originally published in 1885 and 1907, respectively. They contain much useful information for readers interested in the history of fuel technology, particularly ethanol technology.
- Fogler, H.Scott. *Elements of Chemical Reaction Engineering*. Pearson Education International: Saddle River, NJ, 2006. Chapter 7 of this classic chemical engineering text is an excellent discussion of bioreactor engineering and enzymatic reactions.
- Guibet, Jean-Claude. *Fuels and Engines*. Editions Technip: Paris, 1999. Chapter 6 provides a solid discussion of ethanol, and comparisons with other alternative fuels. A very useful reference source.
- Humphrey, Arthur E. and Lee, S. Edward. Industrial fermentation: principles, processes, and products. In: *Riegel's Handbook of Industrial Chemistry* (Kent, James A., ed.) Van Nostrand Reinhold: New York, 1992; Chapter 24. A very useful resource for learning more about fermentation processing, not just for ethanol production, but also for producing many other useful organic compounds.

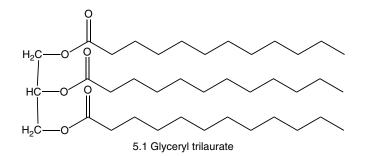
- Lee, Snggyu, Speight, James G., and Loyalka, Sudarshan K. *Handbook of Alternative Fuel Technologies*. CRC Press: Boca Raton, FL, 2007. Chapters 10 and 11 discuss ethanol, from corn and from lignocellulose feedstocks, respectively.
- Lorenzetti, Maureen Shields. *Alternative Motor Fuels*. PennWell: Tulsa, OK, 1996. Though some of the statistical information is now dated, this is still a useful introductory book on this subject. Chapter 2 provides a good history of alternative fuels, and Chapter 6, a good overview on ethanol.
- Minteer, Shelley. *Alcoholic Fuels*. Taylor and Francis: Boca Raton, FL, 2006. Chapters 4, 5, 7, and 8 provide useful information on ethanol from corn, as well as on using ethanol in blends such as E10 and E85.
- Mousdale, David M. *Biofuels*. CRC Press: Boca Raton, FL, 2008. Many of the chapters of this book particularly Chapters 1, 3, 4, and 5 provide very useful technical information on ethanol, including historical development, production from cellulosic feedstocks, and economics.
- Pimentel, David. *Biofuels, Solar and Wind as Renewable Energy Systems*. Springer: New York, 2008. Numerous chapters of this useful book relate to ethanol fuels, including much good information on the Brazilian experience.
- Ramage, M.P. and Tilman, G.D. *Liquid Transportation Fuels from Coal and Biomass*. National Academies Press: Washington, 2009. This book represents the most up-to-date study on this topic, with much useful information on biofuels, including ethanol.

# 5.1 Biosynthesis of plant oils

Plants produce starch from glucose to store energy for future requirements. Plants and animals have a second energy-storage mechanism, synthesis of fats and oils. Plants may have evolved two mechanisms for energy storage because of differences in energy density. Heat of combustion values for starch are -17.5 MJ/kg or -26.2 MJ/l. Comparable values for peanut oil are -33.7 MJ/kg and -33.5 MJ/l. In the main body of the living plant, mass or volume are not usually crucial parameters, and storage of energy as starch, with relatively low energy density, does not become an issue. In storing energy for future generations, the amount of energy that can be packed into the limited volume available in nuts or seeds is critical. Here oils provide a significant advantage relative to starch. Fats and oils represent a subdivision of the broad category of biologically important compounds called lipids. Lipids are characterized as being insoluble in water, but generally soluble in common organic solvents, such as chloroform or diethyl ether. The family of lipids includes many diverse kinds of compound, including beeswax, cholesterol, and oil of turpentine.

Fats and oils are esters. In the special case of fats and oils, the alcohol fragment is 1,2,3-propanetriol, almost always known by its common name glycerol, or by the even older common name, glycerine. The acid fragments are long-chain aliphatic acids, collectively called fatty acids. These acids could be almost any aliphatic acid larger than butyric acid, but in biologically important materials they typically contain 12 or more carbon atoms. Esters of fatty acids with glycerol are called glycerides. Three families of glycerides exist, depending on whether one, two, or all three of the hydroxyl groups in glycerol have been esterified. These families would be known, respectively, as mono-, di-, or tri-glycerides. In plants, the overwhelmingly dominant form is the triglyceride [A]. Mono- and di-glycerides are important only in the digestion of fats. Simple triglycerides are ones in which all three fatty acid segments are identical; in mixed triglycerides, the -OH positions in the glycerol are esterified by different fatty acids. Mixed triglycerides dominate among plant products. Triglycerides solid at 20 °C are classified as fats; those liquid at this temperature are oils. Generally, fats contain saturated fatty acid chains, while oils contain unsaturated ones. Animals usually store energy as fats, while plants store energy as oils.

In a triglyceride, even one composed of three different fatty acids, the three acid chains will lie reasonably parallel to each other, (e.g. glyceryl trilaurate, (5.1).)



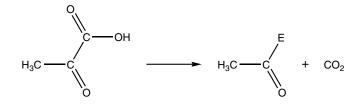
The way in which new pencils lie side-by-side in a package provides an analogy. This structure allows the individual molecules to pack together, held together by van der Waals or London-force intermolecular interactions (discussed in more detail in Chapter 9). These represent the weakest kinds of intermolecular interaction, but the large size of the molecules gives a large surface area over which such forces can operate. These molecules are solids at room temperature, albeit of relatively low melting point. Most kinds of tallow (i.e. fat obtained from cattle and sheep) melt in the range 40-46 °C, for example.

It is possible that there can be one or more double bonds somewhere in the fatty acid chain. The presence of a double bond gives rise, first, to the possibility of cis-, trans- isomerism across the double bond [B]. Second, because free rotation cannot occur around a double bond, its presence puts a permanent "kink" into the chain. More than one double bond can occur in a chain; such compounds are called polyunsaturated [C]. When the fatty acid chains are kinked, the molecules cannot align so well as in the case of saturated chains, nor take advantage of the neat, pencillike alignment of saturated chains to enhance intermolecular interactions. Thus, triglycerides with unsaturated fatty acids can be liquids at room temperature. This behavior follows that of the parent acids. Saturated fatty acids of 12 to 20 carbon atoms have melting points ranging from 44 to 75 °C, increasing as number of carbon atoms increases. Unsaturated fatty acids have much lower melting points; even one double bond can reduce the melting point by several tens of degrees relative to the parent saturated acid. The unusual arachidonic acid, of 20 carbon atoms but with four double bonds in the chain, has a melting point of -50 °C, some 125 °C lower than the saturated arachidic acid [D].

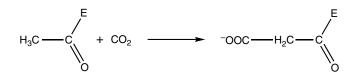
About 200 fatty acids occur in nature. Considering the possible combinations of 200 acids taken three at a time in mixed triglycerides, the possible different arrangements of the three acids at the C1, C2, and C3 positions of the glyceryl residue, and that in many of these triglycerides the C2 position is asymmetric, giving rise to optical isomerism, there could be in excess of 30M different fats or oils. However, in the context of fuel chemistry only a few key points need be kept in mind: the fatty acids mostly have 12 to 20 carbon atoms, almost invariably an even number of carbon atoms (counting the carboxyl carbon), and the double bonds are most often in the *cis*-configuration.

Plants store oils in seeds or nuts to provide a source of energy that the nextgeneration embryonic plant can use for nutrition until it develops to a point at which it can get its own photosynthetic processes started. During that time, the oils are converted to carbohydrates and proteins, in reactions driven by ATP. Many of the common cooking oils come from plant seeds or nuts, including olive oil, canola (rapeseed) oil, and peanut oil. Mature plants do not usually use oils as an energy store. Consequently, the oil content in plant tissues other than the nuts and seeds is quite low [E].

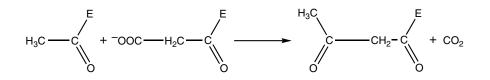
Biosynthesis of fats and oils involves enzyme catalysts. As with photosynthesis and degradation of glucose, we are not concerned about the identities of many of the enzymes involved, nor about their structures. Plants produce sugars during photosynthesis to use them in the synthesis of other compounds important in the plant's life process. Biochemical degradation of glucose to pyruvic acid was discussed in Chapter 4. Pyruvic acid can undergo several chemical fates, including its conversion to ethanol during fermentation or to  $CO_2$  during respiration. Pyruvic acid also serves as a starting point for synthesis of fats and oils. The reaction sequence begins with the characteristic decarboxylation of an  $\alpha$ -keto acid:



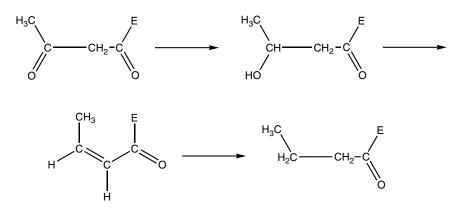
In this equation and those that follow, the symbol **E** denotes an enzyme. Decarboxylation thus leaves an acetaldehyde residue attached to an enzyme. This product can add a carboxyl group to the methyl carbon, in a reaction facilitated by ATP:



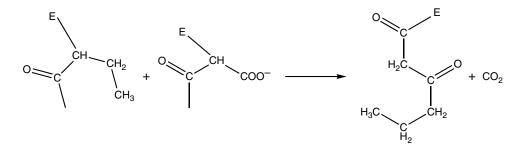
Later, the reaction



occurs, producing a chain of four carbon atoms attached to an enzyme. NADPH serves as an electron carrier and a reducing agent. In the presence of NADPH, the carbonyl carbon not attached to the enzyme becomes reduced to an alcohol. Then, in a sequence of steps, the alcohol is dehydrated to an alkene, and the alkene is reduced.



The final product of these reactions has a four-carbon chain. It can, and does, undergo reactions similar to those shown above.



Another round of carbonyl reduction, alcohol dehydration, and alkene saturation produces a six-carbon chain. The next sequence gives an eight-carbon chain, and another ten, and on up to a chain of 16 carbon atoms, palmitic acid [F]. These reactions began with a two-carbon fragment from decarboxylation of pyruvic acid; chain growth continues by adding two carbon atoms at a time. The consequence is that almost all naturally occurring fatty acids have an even number of carbon atoms. Chain growth often terminates with 16 carbon atoms. After that, other biochemical processes modify the chain length, introduce double bonds into the chain, or do both.

Biosynthesis of the glyceryl fragment involves dihydroxyacetone 3-phosphate. With the intervention of NADPH, dihydroxyacetone 3-phosphate becomes reduced to glycerol 3-phosphate.



Then, fatty acid residues from that biosynthetic pathway are added sequentially in enzyme-catalyzed reactions, forming mono-, then di-, and finally tri-glycerides.

	Canola	Copra	Cotton	Palm	Peanut	Soy
Density, 20 °C, kg/l	0.916	0.915	0.915	_	0.914	0.915
Kinematic viscosity, 20 °C, mm <sup>2</sup> /s	77.8	29.8*	69.9	28.6†	88.5	28.5*
Melting range, °C	-2 to 0	20 to 28	-4 to 0	23 to 27	-3 to 0	-29 to -12
Cetane rating	32-36	40-42	35-40	38-40	39-41	36–39
Heating value, MJ/kg	37.44	37.41	36.78	36.51	36.68	36.82
Heating value, MJ/l	34.30	34.23	33.66		33.52	33.73

Table 5.1 Properties of selected vegetable oils [1].

\*At 38.5 °C. †At 50 °C.

## 5.2 Direct use of vegetable oils as diesel fuel

Rudolf Diesel's first patent application (1892) included use of fats and oils as fuels for his engine. At the Paris Exposition of 1900, Diesel publicly demonstrated the operation of his engine on a vegetable oil [G], specifically, peanut oil. Beginning in the 1920s, palm oil and cottonseed oil were used in some African countries, such as what was then the Belgian Congo [H], as fuel for stationary diesel engines, as well as in trucks and buses. Direct use of vegetable oils as diesel fuel represents one of the simplest ways of using these materials as fuels. Of course they could also be burned directly as a heat source or to raise steam, as a "bio fuel oil" [I]. Normally plant seeds or nuts are dried, then crushed, and finally pressed to expel the oil. The liquid is referred to as crude pressed oil; the solid is called press cake or oil cake. This solid by-product has value as animal feed. Treating the crude pressed oil with steam precipitates any free fatty acids and phospholipids (compounds structurally related to triglycerides but in which one of the fatty acid chains is replaced by a di-ester of phosphoric acid), which can then be removed by centrifugation. The product at this stage is called degummed oil. If the oil is to be used as food or in cooking, a variety of other treatments is applied to ensure its purity. When the oil is used directly as diesel fuel it is sometimes called straight vegetable oil (SVO). In chemical and fuel processing, simplicity is a paramount virtue. Therefore it is worth considering why oils are not ordinarily used directly as diesel fuels, but rather are converted to the fuel now called biodiesel.

Table 5.1 summarizes some of the important properties of SVO with respect to use as a fuel [1].

On a mass basis, heating values of vegetable oils run some 10–15% lower than conventional diesel fuel derived from petroleum (i.e. petrodiesel). This results from the presence of oxygen atoms in the oil molecules. As explained in Chapter 4, oxygen atoms in a molecule reduce the heat of combustion relative to a hydrocarbon of comparable structure and molecular weight. On a volumetric energy basis, though, the comparison is not so unfavorable, thanks to the relatively high densities of the vegetable oils. In energy per unit volume, e.g. MJ/l, vegetable oils are only about 5% lower than petrodiesel. For petrodiesel, heating values are about 42–44 MJ/kg on a mass basis, and 35–37 MJ/l on a volumetric basis.

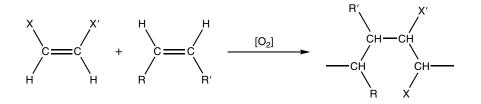
Cetane ratings, which measure the tendency of the fuel to undergo auto-ignition (discussed in Chapter 15), typically range from the low 30s to the low 40s for vegetable oil, whereas a value of  $\approx$ 50 is desirable for diesel engines used in automobiles and light trucks. Petrodiesel usually has cetane ratings from 40 to 60.

Vegetable oils have higher viscosity at a given temperature than does petrodiesel, by an order of magnitude. As temperature drops, the viscosity of vegetable oils increases more rapidly than that of petrodiesel. Heating vegetable oil reduces its viscosity, but even so petrodiesel holds the advantage. For example, canola oil at 50 °C has a viscosity higher by a factor of five than petrodiesel at 20 °C. The relatively high melting temperature of these oils creates problems in cold weather. For example, the cold filter plugging point (CFPP) of any vegetable oil is higher than petrodiesel. The CFPP represents the maximum temperature at which 20 ml of fuel stops flowing through a filter within a specified time. Petrodiesel has CFPP values in the range -10 to -30 °C, below, or at best overlapping with, melting temperatures shown in Table 5.1.

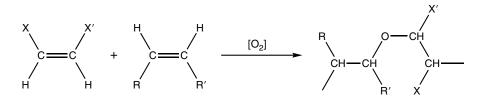
Unlike petrodiesel, which can be distilled completely, only about 20% of vegetable oil can be distilled before the temperature in the distilling flask becomes so high that it causes thermal decomposition of the sample. In processing oils, this is not an issue, because they are not distilled as part of the production process. However, this tendency to break down at high temperature suggests that vegetable oils could form carbonaceous deposits in the engine at combustion temperatures.

Vegetable oils have greatly different materials compatibility than petroleum-derived fuels. Any parts of the fuel system likely to come in contact with the liquid fuel are of concern, especially elastomers that serve as seals or hoses. Vegetable oils are not compatible with, e.g. natural rubber, nitrile rubber, and polypropylene.

Prolonged storage of liquid fuels in air can lead to formation of highly viscous, oligomeric gums. Gums cause several problems when the fuel is used, including accumulating on internal parts in fuel pumps, blocking fuel injectors or nozzles, and piston-ring sticking. Gums form via oligomerization at double bond sites. In petroleum-derived fuels these double bonds are present in alkenes. Oxygen can facilitate gum formation, either by acting to initiate oligomerization that forms carbon–carbon bonds:



or via processes that form carbon-oxygen-carbon linkages:



Double-bond sites in the fatty acid chains of plant oils provide excellent opportunities for these reactions to occur. In other applications of plant oils, we *want* them to oligomerize to gum-like adherent films on surfaces. Linseed oil, for example, can be used to form a hard, nearly impervious finish on fine furniture or the wooden stocks of firearms. Plant oils used in this application are known as drying oils [J]. Oil-based paints contain plant oils – linseed oil has again been a prime choice – to bond the particles of pigment together as the paint dries on exposure to the atmosphere.

Comparisons of vegetable oil with petrodiesel collectively suggest that running modern diesel engines on SVO would be difficult, especially for cold-weather operation. Nevertheless, nowadays interest has developed in using cooking oils, especially oil that has already been used for its original intended purpose, as diesel engine fuel. This material has several names, including waste vegetable oil (WVO) and used cooking oil (UCO). It can often be collected from restaurants, for whom disposing of this material is a problem, at little or no cost. Cooking oil may contain some animal fat, and after use is likely to have some fat from the foods that have been cooked. Other waste products, including bits of bone, meat, and skin, can be present, along with some carbonaceous solids. These oils are normally used for deep-fat frying at 160–185 °C. Heating at this temperature can cause some thermal decomposition of the oil molecules, carbonaceous solids being one of the products. Depending on how carefully, and how cleanly, the restaurant is run, WVO may contain some water. Water forms a separate layer in storage tanks. Bacteria and other microorganisms can grow at the water-oil interface, producing a bio-sludge and, possibly, various organic acids.

Some of the negative characteristics of using SVO or WVO directly as a diesel fuel can be ameliorated by blending with petrodiesel [K]. This practice has been questioned, both for technical reasons – whether doing so would harm the engine or fuel system – and whether it is even legal in some jurisdictions.

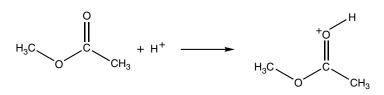
# 5.3 Transesterification of plant oils

Triglycerides are esters. Ester formation is reversible. Using acetic acid and methanol as an example:

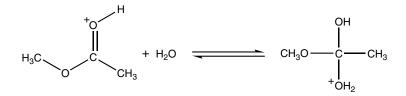


Driving the reaction in reverse represents hydrolysis of an ester. Fats and oils can undergo hydrolysis in a way similar to methyl acetate. The hydrolysis mechanisms are shown using methyl acetate as the example.

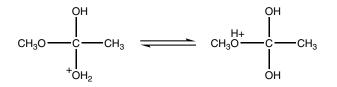
Ester hydrolysis can proceed by two pathways. In the presence of an acid, such as sulfuric acid, the carbonyl group is protonated:



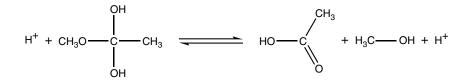
The intermediate is then attacked by a water molecule:



The product has a tetrahedral configuration around the carbon atom that had originally been the carbonyl carbon. Now a proton is transferred:

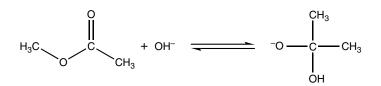


The alcohol is lost, and the proton that had originally come from the acid is liberated.

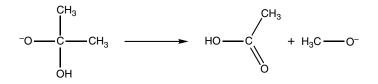


The regeneration of the proton at the end of the reaction allows us to speak of the acid as being a catalyst, since a characteristic of a catalyst is that it is not permanently changed during the reaction. Hence the reaction that has just been illustrated can be called acid-catalyzed hydrolysis of an ester. Often the reaction can be carried out with the ester in solution, in which case the acid acts as a homogeneous catalyst.

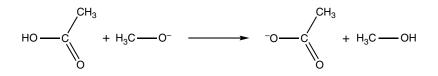
The alternative involves using a base, such as sodium or potassium hydroxide, instead of acid. The reaction begins with an attack by the hydroxide on the carbonyl group:



This intermediate eliminates the alkoxide ion:



Alkoxides are extremely strong bases; the alkoxide ion immediately removes the proton from the carboxylic acid:



The products are the free alcohol and the carboxylate salt of the metal cation that was used with the base, e.g.  $Na^+$  or  $K^+$ . If desired, these sodium or potassium carboxylates could be isolated as one of the final products of the reaction [L]. Liberating the carboxylic acid from the carboxylate can be accomplished easily by acidification.

During hydrolysis of an ester in the presence of base, the hydroxide ion becomes incorporated in the product. It is not recovered or regenerated at the end of the reaction. Since OH<sup>-</sup> is consumed as a reactant, it does not, strictly speaking, function as a catalyst. Thus the reaction is not a base-*catalyzed* hydrolysis; rather, it would be better to speak of base-induced or base-facilitated hydrolysis of the ester.

Because equilibrium exists in ester formation and hydrolysis,

# $RCOOH + HOR' \Rightarrow RCOOR' + H_2O$ ,

it can be driven in either direction by application of Le Chatelier's Principle [M]. Baseinduced hydrolysis provides a way of driving the equilibrium to the left (as written above), taking advantage of the fact that the carboxylate anion will not react with an alcohol to reverse the reaction, i.e.

 $RCOO^- + R'OH \longrightarrow RCOOR' + OH^-$ .

Base-induced hydrolysis is also sometimes referred to as saponification because the resulting sodium or potassium salts are soaps.

In acid-catalyzed hydrolysis, a key step is attack of water on the carbonyl carbon, as shown above. In this reaction, the proton from the water molecule becomes part of the hydroxyl group on the newly produced alcohol, and the –OH from the water molecule becomes the hydroxyl group attached to the carbonyl carbon in the acid. In essence, the water molecule comes apart as in (5.2):

H-OH goes to alcohol goes to acid 5.2 Water molecule parts H—OH can be regarded as the parent compound of a whole family of hydroxyl compounds, e.g. H – OH,  $CH_3 – OH$ ,  $CH_3CH_2 – OH$ , etc. Of course, these are the alcohols. Then by analogy one can consider the acid-catalyzed "alcoholysis" reaction, using methanol as the reacting alcohol:

 $RCOOR' + CH_3OH \Rightarrow RCOOCH_3 + R'OH.$ 

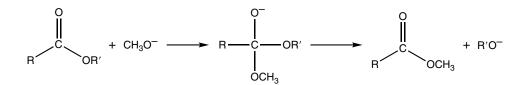
A reaction essentially identical to hydrolysis takes place, but instead of an -OH group attaching to the carbonyl carbon of the acid, an alkoxide group, e.g.  $-OCH_3$ , does so. Instead of the reaction product being a free carboxylic acid, a new ester is produced. This process is called transesterification. Transesterification of fats and oils with methanol will be the key route to producing biodiesel fuel.

### 5.4 Biodiesel

Because at least some of the less favorable characteristics of plant oils derive from the sheer size of the bulky triglyceride molecules, a potential improvement might be achieved by hydrolysis to liberate the fatty acids. The direct use of fatty acids as diesel fuel also has some significant disadvantages. Acids are corrosive. Even though fatty acids are rather weak acids, compared to the mineral acids such as sulfuric or nitric acid, long-term exposure of metals even to weak acids can hasten corrosion. Unlike ethanol, fatty acids are not soluble in water. However, the polar carboxyl group can associate with water molecules via hydrogen bonding, leading to some accumulation of water in the fuel. Hydrolysis of oils to free fatty acids and use of the acids as diesel fuel does not offer a practical solution.

Interest in transesterification of plant oils with methanol or ethanol began in the mid-1940s, after the end of the war. The world-wide availability of cheap petroleum, beginning around 1950, essentially ended interest in the process until the oil price shocks and the so-called energy crisis of the 1970s. In the last several decades, interest in transesterification of plant oils has revived. Usually the alcohol of choice has been methanol, though some have used ethanol. The methyl esters of the fatty acids constitute the material now known as biodiesel.

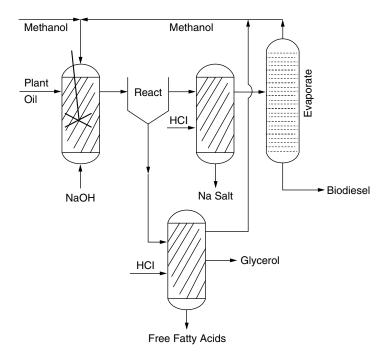
Transesterification of plant oils for production of biodiesel is base-induced, using either potassium or sodium hydroxide. The latter is often preferred because it is cheaper and more easily available. In a non-aqueous reaction system the base reacts with methanol to form methoxide,  $CH_3O^-$ . Methoxide attacks the ester:

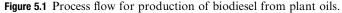


and

$$R'O^- + CH_3OH \rightarrow R'OH + CH_3O^-$$

Figure 5.1 shows a block flow diagram for a biodiesel production process.





The reaction can be carried out in a stirred-tank reactor. Conditions vary somewhat, depending on the choice of the oil, base, and alcohol (in some biodiesel processes, ethanol is used instead of methanol). Generally, the reaction is run for twenty minutes to several hours, at 25–60 °C and ambient pressure, and with an alcohol:oil molar ratio in the range of 5 to 10. The liquid in the reactor separates into two phases, one the primary methyl ester products, and the other mainly glycerol. Separation of these phases results in two processing tracks. The methyl ester products, i.e. the raw biodiesel or "fatty acid methyl esters" (FAME) must be treated with acid – often sulfuric – to neutralize any unreacted hydroxide or methoxide. Washing with water removes soluble salts (e.g. sodium or potassium sulfate). Any excess methanol that might be present in this stream can be recovered by evaporation, collected and recycled. Drying removes any water that might have mixed with the biodiesel. The product is a mixture of purified, washed, and dried FAMEs essentially ready for use as biodiesel. Glycerol is a potential marketable by-product from this process. Untreated glycerol could be sold as-is to a purchaser willing to upgrade the material before use. Alternatively, the glycerol stream could be treated on-site, using acid neutralization to destroy unreacted hydroxide or methoxide, removing the salts, and recovering methanol for recycling.

Table 5.2 compares some key properties of biodiesel with those of conventional petroleum diesel [2]. The standard diesel fuel used in most applications, e.g. for automobiles and light trucks, is No. 2-D. No. 1-D fuel is a refined kerosene. (These fuels are discussed further in Chapter 15.)

As a rule, transesterification improves the cetane rating by about 12 to 15 units compared to the original plant oil. This gives biodiesel a cetane rating of  $\approx$ 50, comparable to petrodiesel. The density of biodiesel appears to be only slightly higher than that of petrodiesel, typically 0.86–0.9 kg/l for biodiesel and 0.85 for No. 2-D diesel.

	No. 1-D petrodiesel	No. 2-D petrodiesel	Biodiesel
Flash point, °C, minimum	38	52	130
Water and sediment, %, max.	0.05	0.05	0.05
90% Distilled, °C	288	338	360
Kinematic viscosity at 40 °C, mm <sup>2</sup> /s, minimum	1.3	1.9	1.9
Ditto, maximum	2.4	4.1	6.0
Ramsbottom carbon residue, %, max.	0.15	0.35	0.05
Ash, %, maximum	0.01	0.01	0.02
Sulfur, %, maximum	0.05	0.05	0.05
Cetane number, minimum	40	40	47

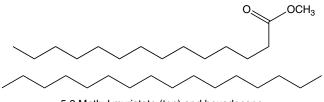
Table 5.2 Comparison of selected properties of No. 1-D and No. 2-D petrodiesel and biodiesel [2].

Probably little or no modification would be needed to the fuel system and engine originally set up to run on petrodiesel for operation on biodiesel. The volumetric energy densities are comparable, typically 35.8 MJ/l for No. 2-D diesel, and 32.8 MJ/l for biodiesel from soybeans.

Standards of biodiesel volatility differ in different countries or regions. As a rule the "90% over" point, that is, the temperature at which 90% of the volume of the liquid has distilled, for biodiesel is higher than for petroleum diesel, e.g. 360 °C vs. 338 °C for grade 2-D petrodiesel. The flash point, the minimum temperature at which there is sufficient vapor over the liquid to sustain a flame, of biodiesel is very high, 130 °C minimum, indicating that this fuel is safe to handle and store from the perspective of fire safety.

The cold-start performance of biodiesel depends on the feedstock used to make it. In optimum cases, biodiesel and petroleum diesel have similar behavior. However, in the worst cases, using a highly saturated feedstock, biodiesel can solidify above  $0^{\circ}$ C. Options available for improving biodiesel performance include leaving some free methanol in the fuel, or blending with a lighter, more volatile liquid such as kerosene. The cold filter plugging point, cloud point, and pour point for biodiesel are all comparable to, or better than, petroleum diesel.

The viscosity of biodiesel is comparable to that of petroleum diesel. This could reasonably be expected, because the molecular structures are so similar; as an example, methyl myristate could be a component of biodiesel, and hexadecane (cetane) of petrodiesel (5.3):



5.3 Methyl myristate (top) and hexadecane

Biodiesel, or its blends with petrodiesel, can be used in existing fuel supply infrastructures and in existing diesel engines without modification. The nomenclature is

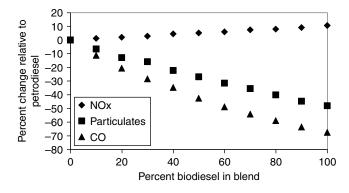


Figure 5.2 The expected changes in engine emissions as biodiesel is blended into conventional petroleum-derived diesel fuel.

analogous to that introduced for ethanol:gasoline blends, except for the use of B as the symbol for biodiesel. For example, B20 represents a blend of 20% biodiesel in petroleum diesel. Biodiesel is biodegradable, so that accidental spills or leakages should not have so severe an impact on the environment as would a petroleum-derived fuel.

Biodiesel contains no sulfur, which means no SOx emissions from combustion. Use of biodiesel tends to reduce emissions of carbon monoxide, particulates, and unburned hydrocarbons. Combining the use of 100% biodiesel with a catalytic converter in the exhaust system, reductions of 45–65% can be achieved, relative to operation on petrodiesel, as illustrated in Figure 5.2.

NOx emissions are increased by  $\approx 10\%$  with biodiesel when it is used as a direct replacement for petrodiesel with no engine modifications. Biodiesel use can potentially reduce NOx emissions if the engine timing (i.e. the point in the engine cycle at which fuel is injected) is retarded relative to operation on petroleum diesel. Doing so, however, invites problems with efficient burning of petrodiesel if the engine is switched back from biodiesel to petrodiesel without readjusting the timing.

Many nations are increasing restrictions on the allowable sulfur content of petrodiesel, with the laudable intent of reducing SOx emissions from diesel vehicles, but doing so has also afforded an excellent example of the law of unintended consequences. Sulfur compounds contribute to the lubricity of petrodiesel, i.e. the ability of the fuel to help reduce friction wear in the fuel system and engine. Removal of sulfur compounds from petrodiesel to reduce emissions can also lead to greater wear as a result of the reduced lubricity. However, biodiesel has higher lubricity than petrodiesel, even with no sulfur compounds present. Even blending biodiesel into petrodiesel enhances lubricity of the blend relative to the unblended petrodiesel. Both the reduced engine emissions and the improved lubricity of vegetable oils relative to petrodiesel were observed and reported by Diesel himself [3,4].

Rudolf Diesel was a remarkable engineer and visionary. It is fitting to end this chapter with a prescient comment Diesel offered a century ago: "The fact that fat oils from vegetable sources can be used may seem insignificant today, but such oils may perhaps become in course of time of the same importance as some natural mineral oils and the tar products are now....these oils...make it certain that motor power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted" [3,4].

#### Notes

- [A] Medical examinations often include measurement of the triglyceride level in the bloodstream. These triglycerides are the same kinds of fat and oil discussed here, and provide an energy source for the body. Elevated levels of triglycerides increase the risk of heart disease, and may signal some underlying medical conditions, such as high blood pressure, hypothyroidism, or kidney disease.
- [B] The stereoisomerism of alkenes is not of much consequence in fuel chemistry, and the *cis*, *trans* nomenclature suffices, particularly for disubstituted alkenes, e.g. those of the type  $R_1HC=CHR_2$ . For more complex structures, e.g.  $R_1HC=CR_2R_3$ , this system is no longer unambiguous, and the more precise *entgegen*, *zusammen* (*E*, *Z*) system is preferable. All modern textbooks of organic chemistry describe the *E*, *Z* system and the rules for its use.
- [C] Some foods, such as seafood and nuts, are touted as containing high concentrations of polyunsaturated fats. This term refers to triglycerides in which one or more of the fatty acid chains contain more than one double bond. Various nutritional and medical benefits have been ascribed to polyunsaturated fats, including their potential for reducing the risk of heart attacks or other cardiovascular problems. However, there are also indications that a diet high in this kind of fat will increase the risk for certain cancers or that the fats will facilitate an existing cancer's metastasis to other sites in the body.
- [D] The saturated parent acid, arachidic acid, is a minor constituent of peanut oil. The unsaturated derivative, arachidonic acid, is a vitally important compound for most mammals, because it has a biochemical role in growth of muscle tissue. In nutrition, this compound belongs to the class of omega-6 polyunsaturated fatty acids.
- [E] Plants produce compounds known as essential oils that often can be isolated by steam distillation. Though produced in small quantities, they have important and commercially valuable applications. Essential oils have no structural similarity to the triglyceride oils; furthermore, substantial structural differences occur among the family of essential oils. Examples include oil of peppermint and oil of spearmint used in food flavoring, eucalyptus oil in medicines, citronella oil used as a mosquito repellent, and the lemongrass and patchouli oils used in perfumes.
- [F] Palmitic acid,  $C_{15}H_{31}COOH$ , would also be called hexadecanoic acid. However, the nomenclature of fats and fatty acids is still dominated by common names. The common names seem to follow little system, except that some, including *palm*itic, often indicate the plant from which they were derived.
- [G] While the word *vegetable* is often used in a limited sense to refer to certain kinds of plant grown for human consumption, the *Oxford English Dictionary* tells us that, as an adjective, vegetable means "of or pertaining to, composed or consisting of, derived or obtained from, plants or their parts ..." The term vegetable oil legitimately refers to oils derived from any kind of plant, regardless of whether we grow it for ourselves to eat or not.
- [H] The former Belgian Congo is nowadays formally known as the Democratic Republic of the Congo, and, until recently, Zaire.
- [I] In the waning days of World War II, the Japanese navy supplemented dwindling supplies of fuel oils with soybean oil from Manchuria. Some reports (though not all)

indicate that the battleship *Yamato*, the largest and most heavily armed battleship ever constructed, used soybean oil to supplement its supplies of petroleum-derived heavy fuel oil in its final sortie in April 1945.

- [J] The use of oils in painting has a long history that probably dates to the eleventh century. Linseed oil, in various degrees of refinement or purity, has been used since about 1400. Giorgio Vasari's *Lives of the Artists*, probably the first book written as a history of art (1550), credits the invention to the painter Jan van Eyk, but probably, as in many developments in art, science, and technology, the development of oil painting was an evolutionary process involving many small improvements by many artists.
- [K] It is fair to say that the literature is not unanimous on this point. As examples, Mousdale mentions blending of vegetable oils and petrodiesel, while Kemp states that the two liquids are totally incompatible. (The books by these two authors are listed in the Recommended reading section below.)
- [L] Soaps are metallic salts of fatty acids. Their usefulness in cleaning derives from the ionic salt end of the molecule being soluble in water, when the metal ion is sodium or potassium, but the long hydrocarbon chain of methylene groups being soluble in other hydrocarbon-like materials, such as grease or oil, or oily films around dirt particles. Reducing the surface tension of the water helps loosen and lift dirt particles. Soaps containing other metallic ions, such as aluminum, calcium, or zinc, are insoluble in water, so are useless as cleansing agents, but some have other applications as, e.g. oil thickeners, lubricating greases, and in face powders.
- [M] Particularly in laboratory-scale work, it is often preferable to synthesize esters from the essentially irreversible reaction of an alcohol with an acid chloride or acid anhydride to avoid having to deal with the equilibrium situation. Going in the opposite direction, base-induced hydrolysis is often preferred because the reaction of hydroxide with the ester is irreversible, again eliminating an equilibrium. When for some reason these tricks of the trade cannot be employed, one can take advantage of Le Chatelier's Principle by, e.g. using a large excess of one of the reagents or removing one of the products – as by distillation – as it forms.

#### References

- [1] Adapted from Guibet, J.C. Fuels and Engines, Editions Technip: Paris, 1999; p. 607.
- [2] Adapted from Kemp, W.H. Biodiesel: Basics and Beyond. Aztext Press: Tamworth, ONT, 2006; p. 64 and 568.
- [3] Diesel, R. The Diesel oil engine. Engineering, 1912, 93, 395-406.
- [4] Diesel, R. The Diesel oil engine and its industrial importance, particularly for Great Britain. Proceedings of the Institute of Mechanical Engineering, 1912, 179–280.

#### Recommended reading

- Goodwin, T.W. and Mercer, E.I. *Introduction to Plant Biochemistry*. Pergamon Press: Oxford, 1983. Chapter 8 provides detailed information on the biosynthesis of fats and oils.
- Hou, Ching T. and Shaw, Jei-fu. *Biocatalysis and Bioenergy*. Wiley: New York, 2008. This book is a collection of edited chapters from an international symposium held in 2006. The first ten chapters deal with various issues in the production and use of biodiesel.
- Kemp, William H. Biodiesel: Basics and Beyond. Aztext Press: Tamworth, ONT, 2006. A solid book on biodiesel, and probably the most thorough and careful treatment of the steps and

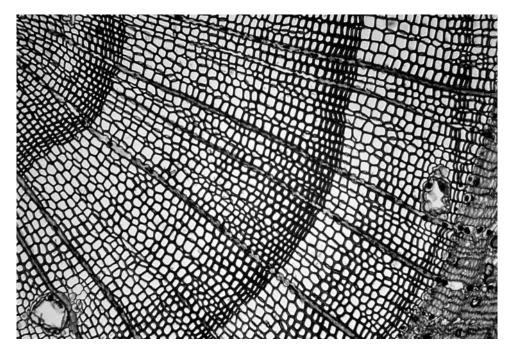
procedures in making one's own biodiesel fuel. Anyone contemplating making biodiesel at home should read this book.

- McMurry, John and Begley, Tadhg. *The Organic Chemistry of Biological Pathways*. Roberts: Englewood, CO, 2005. Chapter 3 includes a discussion of the biosynthesis of fatty acids.
- Morrison, Robert T. and Boyd, Robert N. *Organic Chemistry*. Prentice Hall: Englewood Cliffs, NJ, 1992. All modern introductory organic chemistry texts discuss ester synthesis, hydrolysis, and transesterification. Chapter 20 of this book is a fine example.
- Mousdale, David M. *Biofuels*. CRC Press: Boca Raton, FL, 2008. Chapter 6 provides a solid overview of the chemistry and production of biodiesel.
- Starbuck, Jon. and Harper, Gavin D.J. *Run Your Diesel Vehicle on Biofuels*. McGraw-Hill: New York, 2009. Many books have been published in recent years for laypersons who are reasonably handy with tools and who are interested in producing biodiesel fuel at home and/or converting a vehicle to run on biodiesel. This book has excellent illustrations and checklists of tools needed, and steps to be followed.

Inspecting a collection of various kinds of wood would show considerable variability in physical properties such as color, density, and hardness. Densities range over an order of magnitude, from 110 kg/m<sup>3</sup> for balsa to 1330 kg/m<sup>3</sup> for lignum vitae. Colors vary from the nearly white of some varieties of maple to ebony wood, which lends its name as a synonym for black. A measure of hardness, the Janka test [A], shows again the extremes between lignum vitae, with a hardness of 20000 N, and balsa, at 440 N. Some woods display almost no obvious grain structure, while others have structures so remarkable that they are prized for applications such as making fine furniture. Yet, despite the great range of diversity among woods, all varieties, regardless of botanical or geographical origin, also have many properties in common.

All woods have a cellular structure in which the cell walls are composed of a matrix of biopolymers, discussed later in this chapter. Wood is anisotropic, displaying different physical properties along the three major axes. Anisotropy results from the structure of cellulose in the cell walls, along with the shapes of wood cells and their orientation vis-à-vis the trunk. Wood gains and loses moisture (i.e. it is hygroscopic) as a result of changes in humidity and temperature. Because of the anisotropy, gain or loss of moisture results in unequal swelling or shrinkage along the three axes. Fungi, bacteria, and insects such as termites attack wood. The fact that wood is, as a result, biodegradable has both good and bad points. Obviously it is undesirable when, for example, a wooden structure rots. But, this behavior can also be turned to good use in chemical processing, when fungi or bacteria can be used deliberately to degrade the biopolymers in wood to produce useful chemical or fuel products.

Wood burns readily. Wood must have been one of the first, if not *the* first, fuels used by our pre-human ancestors, dating many millennia back into prehistoric times. Our ancestor *Homo erectus* was using fire at sites in Africa about 1.5 million years ago. On the other hand, wood shows surprising resistance to attack by many chemicals, and has been used in industrial chemistry as a material of construction to take advantage of its chemical or corrosion resistance [B]. Very severe chemical attack is needed to degrade wood rapidly, as experience in the pulp and paper industry shows, where wood is "pulped" by reaction with a mixture of sodium hydroxide and sodium sulfide at  $\approx 175^{\circ}$ C and 0.7 MPa for several hours. Provided that care is taken to protect wood against fire and biodegradation, it can endure for very long periods of time. Wooden artifacts nearly three thousand years old exist, for example, wooden furniture from royal tombs in Anatolia (modern Turkey) that dates to about 800 BC. Not only does wood provide durability in construction, it is



**Figure 6.1** A cross-section of wood illustrates the vascular structure, the system of specialized tissues that transport nutrients and water through the plant.

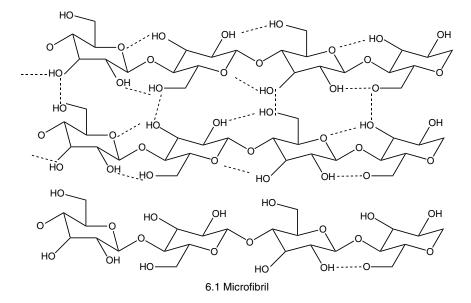
also probably the best thermal insulator of any common building material. Dry wood is also a good electrical insulator.

Wood is the material or "stuff" of woody plants. (Woody plants are sometimes also referred to as higher plants.) Woody plants are those that meet two criteria: first, they are vascular, which means that they have specialized conducting tissues to allow fluid flow through the plant (Figure 6.1).

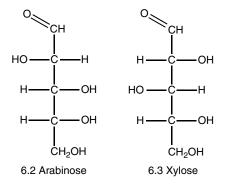
Second, they are perennial, specifically those for which the stem or trunk persists from year to year. Three kinds of plant are classified as woody: trees, woody plants with height exceeding  $\approx$ 7 m and having, usually, a single stem or trunk; shrubs, woody plants under 7 m in height and, often, possessing multiple stems; and lianas, the woody climbing vines.

The principal chemical constituents of wood fall into four broad categories. The first is the polysaccharides. Cellulose, introduced in Chapter 3, is the polymer of glucose featuring  $\beta$ -1,4' acetal linkages. In wood, the glucose monomers in cellulose range from a few hundred to about ten thousand. The cellulose chains pack in a parallel fashion that results in a ribbon-like structure (6.1), called a microfibril.

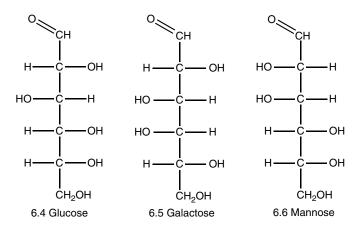
Cellulose typically represents  $\approx$ 50–65% of the polysaccharides in wood. Hemicelluloses make up the remaining 35–50% of the polysaccharides [C]. In the plant cell wall hemicellulose deposits between the cellulose microfibrils, producing a very strong structure. Hemicelluloses are referred to as matrix polysaccharides, from the way in which they provide a matrix for the microfibrils of cellulose. Reinforced concrete provides an analogy [D]. The relative amount of hemicellulose determines whether the solid wood is flexible or rigid. Hemicelluloses incorporate monosaccharides other



than glucose. One type of hemicellulose is based on the aldopentoses, mainly arabinose (6.2) and xylose (6.3):

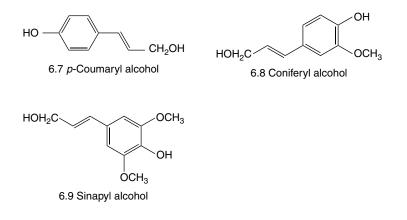


These sugars make forms of hemicellulose known as the xylans, the dominant hemicellulose in hardwoods. A second form of hemicellulose is based on aldohexoses – glucose (6.4), galactose (6.5), and mannose (6.6).

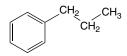


This form, the galactoglucomannans, dominates in softwoods. Unlike cellulose, the hemicelluloses tend to be soluble in dilute alkali and readily hydrolyze in dilute acid to the simple monosaccharides.

Lignin is the third crucial biopolymer in wood, a co-polymer formed from three monomers, p-coumaryl (6.7), coniferyl (6.8), and sinapyl alcohols (6.9).



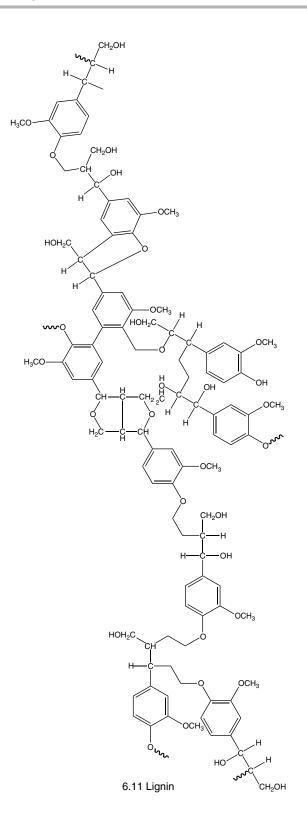
Conceptually, the monomers of lignin can be considered to be derivatives of phenylpropane (6.10).



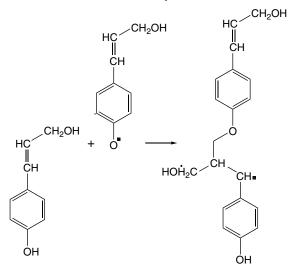
6.10 Phenylpropane

The compounds discussed in previous chapters – proteins, polysaccharides, and lipids – occur in all plants. Lignin occurs only in the woody plants. Lignin provides plants with structural rigidity, one of the reasons why a tree stands up rather than lying limply on the ground. Lignin forms in the living plant as an amorphous polymer. Polysaccharides form in the cell walls first, after which lignification occurs, toward the end of the growth of the cell. Lignin makes up some 15-35% of the woody cell wall. Addition of lignin provides further strengthening of cell walls by interacting with the polysaccharide matrix. These properties can be appreciated by a simple comparison of the feel of wood vs. cotton – wood contains lignin, and cotton does not. Further, lignin is very insoluble and resistant to chemical attack [E], and much less hygroscopic than the polysaccharides, so it serves to protect the cellulose microfibrils and hemicellulose matrix from chemical or biological degradation. Lignin can be separated or extracted from the polysaccharides only with some difficulty.

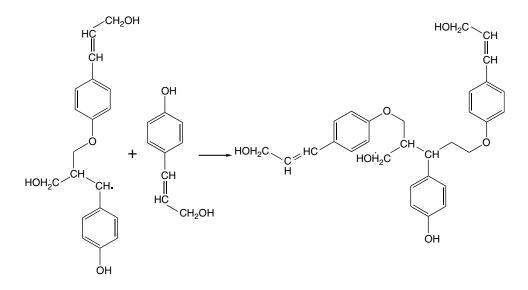
The structure of lignin differs from one species of woody plant to another, as a result of incorporating different proportions of the three monomers. Structure 6.11 gives one representation of a fragment of lignin structure, adapted from [1].



Polymerization of the monomers proceeds via free-radical intermediates. (Free radicals and their reactions are discussed in Chapter 7.) The process is illustrated here using p-coumaryl alcohol as the monomer; in real systems any or all of the monomers could participate in these reactions, and do so in various proportions. The reaction may begin with formation of a radical on the oxygen atom of the phenolic group. This radical reacts with the double bond in the side chain to produce a dimer, containing a new radical site on the benzylic carbon:



Subsequent reaction of the dimeric radical leads to a trimer:

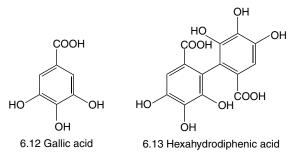


and the process continues to the eventual formation of the polymeric lignin structure.

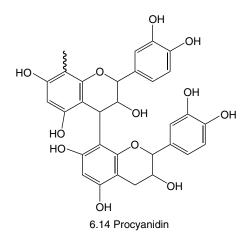
Aside from its occurrence only in woody plants, other aspects of lignin structure are noteworthy. About two-thirds of the carbon in lignin occurs in aromatic structures. Aromatic ring systems possess a special stability, and may be unreactive, or only sluggishly reactive, under conditions in which aliphatic compounds react well. The ether linkages in lignin differ from the glycosidic ethers in polysaccharides. Ethers in lignin are not readily hydrolyzed or otherwise reacted. Thus lignin molecules tend to be much less reactive than the other classes of compound discussed to this point. The relative stability of lignin structures has special importance in the transformation of organic matter to fossil fuels (Chapter 8). Lignin also incorporates the phenolic functional group, which has no role in ethanol or biodiesel chemistry.

The compounds called extractives are materials that can be liberated from wood via steam distillation or solvent extraction. Extractives usually amount to only a few percent by weight of wood, but include a very wide variety of such compounds as, for example, fats, free fatty acids, waxes, resins, tannins, gums, terpenoids, flavanoids, stilbenes, tropolenes, and volatile hydrocarbons.

Tannins have complex, polyphenol structures with molecular weights typically in the range 500 to 3000 Da. These compounds confer the ability of some wood extracts to tan animal skins, i.e. to turn skins to leather. Tannins occur in two groups. Hydrolyzable tannins contain glucose esterified with gallic acid (6.12) or with hexahydrodiphenic acid (6.13).

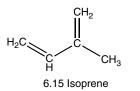


Condensed tannins have oligomeric or polymeric structures, of which the fragment procyanidin (6.14) provides an example.

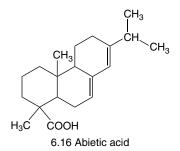


The "squiggle bond" in structure 6.14 denotes the position at which further oligomerization could occur.

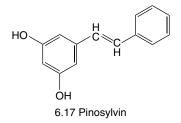
Terpenoids, a family of probably more than ten thousand compounds, derive from a basic five-carbon structural unit whose parent hydrocarbon would be 2-methyl-1, 3-butadiene (6.15), commonly known as isoprene.



Resins derive from triterpenoid acids, for example abietic acid (6.16):



Woody plants produce resins to seal wounds and to guard against fungal attack. Resins oligomerize through their double bonds, forming high molecular weight, slightly soluble (or insoluble) materials like the gums discussed in the context of biodiesel (Chapter 5). Stilbene derivatives come from the parent *trans*-1,2-diphenylethene (stilbene), an example being pinosylvin (6.17):

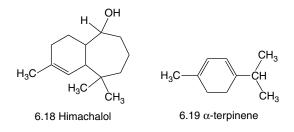


Some stilbenes are toxic to fungi that attack wood; others deter animals from eating the plant. Pinosylvin, for example, acts as a deterrent to hares attempting to eat the shoots of pine trees.

Waxes, which belong to the lipid family, regulate water permeability of leaves and stems. Waxes usually are esters of long-chain alcohols with fatty acids, but may also contain alkanes, long-chain alcohols, and fatty acids. An example is carnauba wax, which derives from Brazilian palm trees and can be represented as  $CH_3(CH_2)_xCOO(CH_2)_yCH_3$ , where x is 22–26 and y is 30–32. Carnauba wax has commercial value in automobile and floor waxes, cosmetics, and in the mixture used to make dental impressions. Alkanes in waxes usually have an odd number of carbon atoms. Some plants contain relatively small hydrocarbons, e.g. heptane, found in turpentine. Very large alkanes –  $C_{27}$ ,  $C_{29}$ ,  $C_{31}$  – occur in plant waxes. Almost all naturally occurring fatty acids have an even number of carbon atoms (Chapter 5). That alkanes in plant waxes have an odd number suggests that they result from decarboxylation of very large fatty acids, e.g.

Nonacosane,  $C_{29}H_{60}$ , found in the waxy layer on cabbage leaves, is an example. During warm, sunny days in summer, plants can release volatile hydrocarbons, such as isoprene. Oxidation of these compounds, facilitated by sunlight, produces a natural form of smog responsible for the haze that is characteristic of some forested regions, such as the Blue Ridge and the Great Smoky mountains in the United States.

Extractives are the components responsible for the characteristic aromas and colors of woods. Some extractives have significant commercial value, such as the so-called naval stores [F], e.g. turpentine and rosin. Turpentine, also known as spirits of turpentine or oil of turpentine, is made by distilling resins collected from pine trees. It serves as a useful solvent for various kinds of varnish and oil, as a thinner or vehicle for paints, and as a paint remover. Rosin, the distillation residue remaining after driving the volatile components from resins, has a wide range of commercial uses, from varnish and printing inks to waterproofing agents and wood polishes. Steam distillation of pine wood yields pine oil, composed of various alcohol derivatives of terpenes, for which himachalol (6.18) serves as an example, and a variety of terpene hydrocarbons, isomers of the formula  $C_{10}H_{16}$ , exemplified by  $\alpha$ -terpinene (6.19).



Pine oil makes a very useful disinfectant; its characteristic odor (which may help mask far more unpleasant odors) may be encountered in hospitals or public restrooms. Pitch is a highly viscous residue remaining from wood pyrolysis [G]. In the days of sailing ships, pitch was extremely valuable to seal the wood planking and for other uses where a tightly sticking, water-resistant material was needed.

Wood contains small amounts of inorganic constituents. These inorganic components were assimilated by the plant and utilized for various biochemical functions. Magnesium, for example, is a key component of chlorophyll. When wood is burned, these inorganics contribute to the formation of a noncombustible residue, ash. There is no ash *in* wood; ash is a reaction product of the various inorganic components of wood during the combustion process. The ash residue typically represents  $\approx 0.1-0.5\%$  of the weight of the dry wood. The dominant components of wood ash are the alkali and alkaline earth elements, particularly potassium, magnesium, and calcium [H].

Wood can be used directly, for timber, furniture, and many other useful wooden artifacts. Alternatively, wood can be burned as a fuel or converted into useful fuel and chemical products. The use of wood or wood-derived materials as fuels occupies the remainder of this chapter. Wood is used in large amounts for products outside the scope of fuel chemistry. Paper products are most noteworthy, but other materials, such as cellophane and rayon, also derive from wood chemistry.

# 6.1 Wood combustion

Use of wood as a fuel extends back to prehistoric times. Wood was the first major fuel to be exploited by humans, and was the dominant fuel world-wide well into the nineteenth century, when it was displaced by coal in Europe and the United States. Wood remains an important fuel in many parts of the developing world, particularly for domestic use. Half the world's population uses various biofuels, including wood, for cooking and other household uses. The wood resource available as feedstocks for combustion or conversion to other fuel products need not be confined only to newly felled trees. Material considered by the forest product industry to be waste, such as bark or pieces of wood too small to be cut in usable lumber, makes useful fuel. Forest litter – the debris of dead branches and felled trees found in forests – constitutes another source of wood fuel.

The calorific value of perfectly dry wood is about 18–21 MJ/kg, depending on the species of tree from which the wood was harvested. Since lignin has a higher heat of combustion than cellulose (26 vs. 18 MJ/kg, respectively), calorific value varies with lignin content. Extractives have still higher calorific values, but their contribution to the total mass of wood is usually low. Nonetheless, resinous woods have a higher calorific value than woods containing little or no resin. Calorific value on a dry basis, in MJ/kg, can be estimated from the equation [3],

$$CV = 17.5 F + 26.5 (1 - F),$$

where F is the fraction of cellulose and hemicellulose in the wood. Calorific values for perfectly dry wood show that it can provide about 75% of the heat obtainable from good-quality coal, and about 40% of that from petroleum. However, "perfectly dry" wood is extremely difficult to obtain in practice, since all wood contains an appreciable amount of moisture as harvested, as much as 40–45% for some softwoods. Burning freshly harvested wood – so-called green wood – would probably provide only about 5 MJ/kg. Even cut wood that has been carefully sheltered from the weather and has been allowed to dry in air for months might still contain  $\approx 15\%$  moisture, so that the calorific value of air-dried wood might be about 15 MJ/kg.

In several respects, wood is an ideal fuel for pre-industrial or developing societies. It occurs naturally on the Earth's surface, so that technology is not needed to mine or extract it from inside the Earth. Wood, at least in the past, was widely and abundantly available in many parts of the world. Wood can be burned in simple appliances with minimal knowledge of combustion principles; almost everyone with experience in overnight camping or outdoor cooking can attest that, given enough matches and enough patience, practically anybody can get a wood fire going.

Combustion of a solid fuel often proceeds in two stages. Volatile components of the fuel are vaporized by the heat from the flame. They ignite and burn in a homogeneous gas-phase reaction. Then the residual highly carbonaceous solid (char) ignites and burns in a heterogeneous gas-solid reaction. Compared to coals, the proportion of volatile components is usually much higher, up to 80%. This must be considered in adapting existing designs for coal combustion equipment to wood combustion, or in evaluating the possibility of co-firing coal and wood. Any combustor design must insure that the volatiles indeed ignite and burn out completely in the furnace, rather than escaping up the stack.

Wood fires produce significant air pollution in the open or in relatively simple domestic appliances. Volatile compounds escape as the wood is heated to its ignition point. Many of these contribute to the characteristic "smoky" odor noticeable in the clothes or hair of anyone spending time near a wood fire. Some of the volatiles could also have adverse health effects. Incomplete combustion can produce carbon monoxide, which is potentially deadly. Smoke contains fine particles of ash, soot, and partially burned wood.

Inorganic components such as sodium, potassium, magnesium, or calcium react with silicon dioxide, aluminum oxide, and clays to form compounds with relatively low melting points. These low-melting products can deposit inside a furnace to form sticky surfaces that can accumulate yet more ash, as well as retarding heat transfer. In extreme cases, a molten, running slag can form on furnace walls. In fluidized-bed combustion, low-melting ash components can accelerate sintering of the particles in the bed, until the sintered particles become so large that they can no longer be fluidized. The potential for fouling heat-transfer surfaces, slagging, and sintering must be considered in designing and operating equipment for burning wood or other biomass resources.

In one sense, wood is a renewable energy source, because a new tree can be grown to replace every one that was harvested. Unlike corn, sugar cane, and crops grown for oils, the next generation tree, replacing one that had been harvested, does not grow to maturity in a year. Abundant evidence, both from history and from current experience, shows that large-scale cutting of trees for domestic or industrial fuel leads to destruction of forested areas. Such deforestation brings with it a host of other environmental problems. A sustainable strategy for assuring a renewable supply of wood relies on cutting in rotation from woodlots specifically grown and managed for the periodic harvesting of wood, a practice known as coppicing. Hybrid poplars and willows are good candidates for coppicing. Depending on the specific kind of tree being grown, harvesting can be done on cycles of about seven to twenty years.

## 6.2 Wood pyrolysis

### 6.2.1 Charcoal

Someone – quite probably several different someones independently of one another – must have observed occasions in which a fire did not consume the wood completely, but left behind a black, brittle residue, which, if it were retrieved and later re-ignited, was itself a good fuel. This we now call charcoal. Eventually it was understood that the charcoal residue from a fire came about because there was insufficient oxygen (air) to consume the wood completely. From that understanding came the recognition of the possibility of making charcoal deliberately by heating wood in the absence of air, or burning wood under severely air-limited conditions. Along the way, it was also realized that some of the volatile materials "cooked" out of wood during its conversion to charcoal also had valuable uses.

Production of charcoal, along with the chemical products to be discussed in the next section, involves pyrolysis, i.e. decomposition of compounds through application of heat. Because pyrolysis converts wood to a highly carbonaceous material, charcoal, the

process is also known as carbonization. Since volatile compounds are driven off, but the residual non-volatile material is obviously quite altered, yet another name for the same process is destructive distillation. Active thermal decomposition of wood begins around  $250^{\circ}$ C. Industrial carbonization is done at  $\approx 500^{\circ}$ C.

Charcoal is an excellent fuel. It has a very high calorific value, about 30 MJ/kg, equivalent to the best of the coals, and double the value of air-dried wood. Cellulose, hemicellulose, and lignin have highly oxygenated structures. During carbonization, many components driven off by the heating take a good proportion of the oxygen with them. Thus the calorific value of the residual charcoal is higher than that of the wood feedstock. The sulfur content is nil; sulfur oxide emissions are not a problem. Charcoal burns with a clean, smokeless flame. These factors make charcoal much preferable to wood for domestic use, as well as for industrial uses, such as firing ceramics, where it is important that the product not be contaminated by products of the fuel combustion. Brick kilns and lime kilns have also been fired with charcoal. A charcoal fire can, however, produce significant amounts of carbon monoxide if care is not taken to supply adequate amounts of air.

Charcoal does not have a characteristic molecular structure the way, e.g. that cellulose does. It does not even have a structure that can be approximated, as do hemicellulose or lignin. Charcoal contains a high percentage of carbon (75–100%). Most or all of the carbon is in aromatic structures. Commercial charcoal comes from destructive distillation operated at 400–500°C. It can contain up to 25% of organic compounds that have not fully carbonized, and which may contain hydrogen and oxygen. Charcoal yield depends on the wood used as feedstock, its moisture content, and on specific process conditions, but in best cases could be in the range of 30 to 40%.

Production of charcoal relies on burning a portion of the available wood to provide the heat necessary to carbonize the remainder. Therefore the process is inherently wasteful, and probably in pre-industrial societies was exceptionally so. In its simplest form, charcoal production involved creating a heap of wood, on the ground or in a pit, igniting the wood, and allowing the heat to carbonize the unburned wood. This rough and ready approach probably attained temperatures of 350–500°C. The yield of charcoal was likely to be no better than about 25% of the initial charge of wood, possibly as bad as 10%. Modern engineering concepts of process control and quality control had no application in early charcoal making, so both yield and quality of product varied from one batch to the next. When wood is carbonized with some care, as in permanently constructed brick kilns used in Thailand, charcoal yield increases to about 40%, and production cost per net tonne of charcoal is lower by about one-third relative to more primitive processes.

In addition to direct use as a fuel, charcoal has been used since ancient times as a reducing agent in metallurgy. The first application was in production of copper, for use in bronze alloys, and then production of iron. Charcoal has several virtues in this application, containing virtually no impurities – such as phosphorus or sulfur – that would contaminate the metal, and being able to provide temperatures of  $\approx 2000$  °C in furnaces with an air draft. Unfortunately, the metallurgical application of charcoal consumed prodigious quantities of wood. Roman copper smelting would have consumed an estimated 5000 ha of forest per year for a net production of 1 tonne of copper per day; an eighteenth-century English blast furnace would have needed about 12000 tonnes of wood to produce 300 tonnes of iron [2]. The expanding metallurgical industry led to extensive deforestation through much of

Europe. Nowadays the only major application of charcoal as a reducing agent is in the Brazilian steel industry.

Wood has a cellular structure, and woody plants are characterized by vascular tissues that provide conduits for fluid flow. When wood is carefully carbonized, the cell walls and vascular "pipelines" can be retained in the solid product. Thus charcoal is often very highly porous. The total surface area of a charcoal sample, including the so-called internal surface that forms the walls of the pores, can be in the range of  $200-300 \text{ m}^2/\text{g}$ . These porous charcoals are especially useful as adsorbents, to purify liquids or gases. Even a crudely prepared charcoal can be of some use in this regard. Much research and development is devoted to preparing special adsorbents, known as activated carbons, having pore sizes and surface areas designed to adsorb specific compounds or classes of compound. Surface areas of activated carbons can exceed  $1000 \text{ m}^2/\text{g}$ . Production of activated carbons from wood (and other feedstocks, including coal) is a growth industry, projected at 5–10% per year. It seems likely to remain so for the foreseeable future, as countries around the world place increasing emphasis on environmental protection or remediation, applications in which activated carbons are vital.

Carbonization drives off moisture, along with a host of low molecular weight organic compounds that derive from the extractives and from pyrolysis of the biopolymers. Condensing vapors from carbonization produces an aqueous solution called pyroligneous acid. It is a dilute solution of up to about 50 small, polar (and hence watersoluble) organic compounds. Of these, the most important, both in terms of yields and of commercial application, are acetic acid, acetone, and methanol. Other products include ethanol and 2-propen-1-ol (allyl alcohol). Carbonization of hardwoods was, at one time, the dominant source of acetic acid, acetone, and methanol, all of which have important chemical uses. However, industrial demand for all three has grown to a point that could not possibly be met by wood carbonization, so alternative processes have been developed for each.

Condensable non-aqueous organic materials also form. These are generically called wood tars, the word tar referring to a complex mixture of organic compounds [I], usually viscous and of high molecular weight, produced by pyrolysis or destructive distillation. Tars can be fractionated into light oils, boiling below 200°C, and heavy tars, boiling above that temperature, and pitch. Light tars tend to be mixtures of aldehydes, carboxylic acids, esters, and ketones. Heavy oil contains a variety of phenol derivatives; one of its uses is as a wood preservative (e.g. for wooden cross ties on railroad tracks), under the name wood tar creosote or creosote oil.

#### 6.2.2 Methanol

Historically, one of the most important compounds recovered from pyroligneous acid was methanol. Its trivial name, wood alcohol, reflects this. Methanol serves as a useful industrial solvent, and as the starting material for industrial synthesis of several organic commodities, such as formaldehyde and acetic acid. The worldwide chemical industry consumes over 40 million tonnes per year. In wood pyrolysis, methanol probably arises from two sources: demethoxylation of lignin and gas-phase reactions such as

 $CO + 2H_2 \rightarrow CH_3OH$ ,

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O.$$

Methanol is also suggested from time to time as a potential motor-vehicle fuel. A discussion of the possible advantages and disadvantages of methanol in this application is deferred to Chapter 21, which introduces the modern industrial synthesis of methanol. Wood pyrolysis cannot hope to keep up even with the current demand for methanol in the chemical industry. The estimated yield from pyroligneous acid was about 20 liters of methanol per tonne of dry wood using hardwood feedstocks, but only about 10 l/t from softwoods. Just satisfying the chemical industry's appetite for methanol would require an annual harvest of 2.5 billion tonnes of dry hardwood worldwide. The situation would be even worse if a demand for fuel-grade methanol were added to its present chemical uses.

## 6.3 Wood gasification

Most of the current demand for methanol is met by making it from natural gas, or specifically methane. While this process is a technological success and is practiced on an immense scale worldwide, it relies on a fossil, rather than renewable, feedstock. Natural gas is a premium gaseous fuel, so it can be argued that converting it to a liquid currently used as a chemical product diverts natural gas out of the fuel markets.

Wood gasification involves reacting steam with the components of wood. An empirical formula for perfectly dry hardwood, without the inorganic constituents and neglecting the small amount of nitrogen (the sulfur content is nil) is  $C_{48}H_{68}O_{32}$ . On the same basis, a formula for softwood would be  $C_{45}H_{62}O_{26}$ . The respective reactions with steam can be written as

$$\begin{split} & C_{48}H_{68}O_{32} + 16\,H_2O \rightarrow 48\,CO + 50\,H_2, \\ & C_{45}H_{62}O_{26} + 19\,H_2O \rightarrow 45\,CO + 50\,H_2. \end{split}$$

Two important, but very different, points need to be considered in connection with this process. First, the reaction of carbon-containing materials with steam is both very important and very versatile, because it can proceed for virtually any feedstock that contains carbon [J]. Aspects of this reaction recur in discussions of natural gas, petroleum, and coal chemistry. Second, even if wood really could be considered a simple compound, as suggested by these empirical formulas, the reaction is never this clean in practice. Some of the wood may pyrolyze, and some may burn, before the reaction with steam. Thus an array of other gaseous and condensable products will form.

The important, and desired, product of wood gasification is a mixture of carbon monoxide and hydrogen, called synthesis gas. The name derives from the fact that synthesis gas can be used to synthesize highly useful products, including methanol and liquid hydrocarbons. The chemistry and technology of these syntheses is discussed later, in the context of the present-day production of methanol from natural gas and liquid hydrocarbons from coal (Chapter 21). Conversion of wood to synthesis gas provides a potential route to production of large quantities of methanol from biomass rather than fossil fuel resources, and in far higher amounts than could be obtained by isolating methanol from pyroligneous acid.

Methanol synthesis from wood gasification involves the reaction

$$CO + 2H_2 \rightarrow CH_3OH.$$

How this reaction is performed on an industrial scale, reaction conditions, and catalysis are discussed in Chapter 21. Inspection of the previous two equations shows a mismatch in the stoichiometry of the synthesis gas produced from wood and that required for methanol synthesis. Based on these empirical formulas for wood, gasification produces synthesis gas with a H<sub>2</sub>/CO ratio of  $\approx$ 1, but methanol synthesis requires a ratio of 2.0. Fortunately, a relatively easy way exists to solve this apparent problem, the water-gas shift reaction:

$$CO + H_2O \Rightarrow CO_2 + H_2.$$

The water-gas shift is an equilibrium process, which makes it possible to apply Le Chatelier's Principle to drive the reaction in either direction, as needed, raising or lowering the  $H_2/CO$  ratio to any desired value, from pure CO to pure  $H_2$  [K]. Thus the route from wood (or other biomass) to methanol is gasification, followed by the water-gas shift, followed by methanol synthesis.

This approach to biomass conversion to methanol is the first example of a strategy of extraordinary power in fuel chemistry. With the appropriate reactor design, virtually any carbon-containing feedstock, biomass or fossil, can be converted to synthesis gas. Then, via the water-gas shift, the  $H_2/CO$  ratio in the synthesis gas can be "shifted" to any desired value. Finally, the shifted gas can then be used to produce a wide variety of fuels and industrial chemicals, including methane, methanol, and a range of hydrocarbon liquids.

The other solid feedstock used for gasification is coal (Chapter 19). Wood gasification requires different fuel preparation equipment, because coals are usually brittle solids, whereas much wood and other forms of biomass are fibrous. However, once the appropriate size reduction and drying have been done, wood offers the advantages of lower requirements for steam and oxygen, and less shifting of the gas downstream. Further, wood contains no sulfur, eliminating requirements for downstream H<sub>2</sub>S removal from the gas. The economics of feedstock collection and shipment to a plant limit the size of a wood gasification facility. Estimates of the maximum radius over which it is economically feasible to collect and ship wood to a central facility vary with the assumptions made in the economic model, but generally lie in the range of 50 to 160 km.

In some countries, biomass is counted as contributing zero carbon dioxide emissions, on the principle that the growth of the next crop will remove  $CO_2$  from the atmosphere equivalent to that emitted by consuming this year's crop. Without carbon dioxide capture technology, a coal gasification plant can be a large source of  $CO_2$  emissions. Combining coal and wood in the same facility, either via co-gasification in the same reactors, or separate, parallel trains of coal and wood gasifiers, represents a strategy for reducing the  $CO_2$  emissions (or the so-called carbon footprint) of a gasification facility.

## 6.4 Wood saccharification and fermentation

Polysaccharides in wood can be cleaved to their simple pentose and hexose constituents. Subsequently, hexoses can be fermented to ethanol by enzymes from yeasts. The principles are no different from those discussed in Chapter 4. In practice, the challenges are the separation of cellulose from the other wood constituents, and then hydrolysis of cellulose to hexoses. And, pentoses from hydrolysis of hemicelluloses do not ferment. The Bergius–Rheinau process [L] involves countercurrent extraction of dried wood chips with 40–45% aqueous hydrochloric acid. The resulting solution contains about 25% of sugars as various oligosaccharides, obtained in about 65% yield. Vacuum distillation recovers the acid for recycling through the process, and leaves an aqueous solution of sugars. Spray-drying recovers the sugars as a solid; subsequent hydrolysis in 2% aqueous acid produces monosaccharides for feeding to a fermentation reactor. (Sugars from this process could also be used for human consumption.)

The Madison process reacts sawdust or wood shavings with 0.5% aqueous sulfuric acid at 130–180°C and 1 MPa. Residual acid remaining in the sugar solution, which is about 5% sugars and 5% acid, is neutralized with calcium hydroxide. The process gives a sugar yield of  $\approx$ 50% of the amount of cellulose, which then provides about 250 liters of ethanol per tonne of dry wood. The Bergius–Rheinau process can yield up to 325 l/t.

### Notes

- [A] The Janka test measures the force required to embed an 11.3 mm steel ball to a depth equal to half its diameter. A practical application of Janka hardness data is in selection of woods to be used as flooring.
- [B] Wood also has serious drawbacks when used as a material in fuel or chemical processing. When wood is brought into contact with concentrated aqueous solutions of almost any compound, it loses water to the solution, dehydrating and, consequently, shrinking badly. Hot aqueous acids or bases will slowly hydrolyze the cellulose and hemicellulose in the wood.
- [C] The term hemicellulose was coined in the 1890s by the Swiss agricultural chemist Ernst Schulze (1840–1912), who mistakenly thought that hemicellulose was a smaller, less polymerized version of cellulose, the prefix hemi- meaning "half." Although we now know that Schulze's structural model of hemicellulose was incorrect, the name carries on.
- [D] Reinforced concrete is concrete to which another material has been added to improve the overall strength. Normally, concrete is extremely strong in compression, but is quite weak when subjected to tension. The purpose of the reinforcement is to enhance tensile strength. Most commonly steel rods or grids are used for this. Steel has very good tensile strength. For a reinforced concrete piece, the concrete provides the compressive strength and steel the tensile strength. Worst case, if the concrete fractures, the reinforcing material can help to hold the piece together.
- [E] Here we see the chemical consequence of the reactivity of the ether linkage in acetals and hemiacetals vs. that of regular ethers. Ethers represent a significant contribution to the bonding between monomers in the lignin structure. Their resistance to hydrolysis contributes significantly to the low reactivity of lignin compared to that of the polysaccharides.
- [F] In the days when most ships were made of wood, a variety of products useful in, or on, ships was made from pine wood. Because of their connection to the thencommon wooden ships, these products became known collectively as naval stores. They include pitch, used as a sealant; turpentine, useful as a solvent and as a vehicle for paint; and rosin, used to make varnishes, sealing wax, and wood polish.

- [G] Pitch is a term in fuel chemistry the word coke is another example that occurs in connection with several fuel feedstocks. All pitches are highly viscous, sometimes appearing solid at ambient temperature, and are usually very aromatic, materials useful as binders or sealants. But pitch derived from wood is not identical, in physical properties or chemical composition, to pitch from petroleum residues, nor to pitch derived from coal tars.
- [H] The potassium content makes wood ash valuable for saponification (base-induced hydrolysis) of fats and oils to make soap. Persons who use wood for home heating and cooking can save the ashes and produce potassium hydroxide solution by leaching the ashes with hot water. If they also save used cooking oils and fats, reaction of these materials with potassium hydroxide provides a perfectly useful (and essentially free) source of home-made soap. The most important aspect of the process is to ensure that no free KOH which is very caustic and will remove not only dirt and stains but also skin and the flesh underneath remains in the soap.
- [I] Like pitch, mentioned above, tar is another word that occurs repeatedly in fuel chemistry. It usually refers to a viscous, aromatic product of pyrolysis, but its composition and physical properties vary widely, depending on the feedstock and on the pyrolysis conditions.
- [J] This is not to imply that various kinds of carbonaceous feedstocks can all be gasified in the same piece of hardware. The design of the reactor must be mated to the characteristics of the feedstock. Among other things, the physical state of the feedstock – solid, liquid, or gaseous – has significant impact on the design and mechanical operation of the reactor. This is revisited later in the book, in discussing steam reforming of natural gas and coal gasification.
- [K] In industrial processing it is usually not necessary to "shift" the entire gas stream, but only enough of the gas to give the desired  $H_2/CO$  ratio. Some fraction of the synthesis gas can be allowed to bypass the shift reactor. This point is revisited in Chapter 20.
- [L] Developed by Friedrich Bergius (1884–1949), today better known for his work in liquefaction of coal, and who is discussed again in Chapter 22.

#### References

- [1] Goodwin, T.W. and Mercer, E.I. Introduction to Plant Biochemistry. Pergamon: Oxford, 1983; page 69.
- [2] Smil, Vaclav. Energy in Nature and Society. MIT Press: Cambridge, 2008; page 191.
- [3] Modified from Tillman, David A. Wood as an Energy Resource. Academic Press: New York, 1978; page 68.

#### **Recommended reading**

- Breitmaier, Eberhard. *Terpenes*. Wiley-VCH: Weinheim, 2006. A short monograph on these compounds, recommended for those seeking more detailed information on this extensive family of plant components.
- Goodwin, T.W. and Mercer, E.I. *Introduction to Plant Biochemistry*. Pergamon Press: Oxford, 1983. This excellent book has a wealth of additional information on the composition, biosynthesis, and reactions of the many types of compound discussed in this chapter.

Higman, Christopher and van der Burgt, Maarten. *Gasification*. Elsevier: Amsterdam, 2008. Chapter 5 of this fine book discusses aspects of biomass gasification.

- Mauseth, James D. *Botany*. Jones and Bartlett: Sudbury, MA, 1998. Chapter 8 has a useful discussion, supplemented by numerous excellent illustrations, on the structure of wood from a botanical perspective.
- Ryan, John Fuller. *Wartime Woodburners*. Schiffer Military History: Atglen, PA, 2009. The well-known adage that "necessity is the mother of invention" is amply illustrated in this book, which discusses the use of gas produced from wood as a motor vehicle fuel in effect, how to convert a vehicle (including motorcycles) into a rolling wood gasifier.
- Tillman, David A. *Wood as an Energy Resource*. Academic Press: New York, 1978. Though some sections, on current uses and forecasts, are now out of date, this book remains a very useful review of the applications of wood as fuel.
- Young, Raymond A. Wood and wood products. In: *Riegel's Handbook of Industrial Chemistry*. (Kent, James A., ed.) Van Nostrand Reinhold: New York, 1992; Chapter 7. A comprehensive review of the reactions and processes of wood in the chemical industries, with much useful information on processes such as pulp and paper manufacturing not covered in this book.

Species in which carbon has a valence other than its customary four form as intermediates in reactions, and usually display high reactivity. Five kinds of reactive intermediate are known: carbonium ions [A], in which carbon has a valence of five, as in the methanonium ion,  $CH_5^+$ ; carbocations, radicals, and carbanions, in which carbon has a valence of three; and the divalent carbenes. Of these, carbocations and radicals are the most important in fuel chemistry.

# 7.1 Bond formation and dissociation

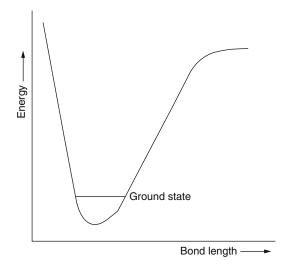
When the ultimate effect of a chemical reaction is breaking of one or more bonds, the overall reaction will invariably be endothermic. When bond-breaking is one in a series of elementary steps in a reaction mechanism, that individual step is also invariably endothermic, even if the overall reaction is exothermic.

Suppose there are two generic atoms, A and B, that approach each other from an infinite distance apart (on an atomic scale, this "infinite" distance could be, say, a millimeter). At first, they have no interaction. As they approach to a distance at which they can interact, the potential energy of the A–B system becomes lower than that of the two separated A and B atoms. The potential continues to drop, until a bond has formed between them. Attempts to decrease the A–B distance even further cause the potential to shoot up rapidly, because of repulsion between electron clouds on the two atoms.

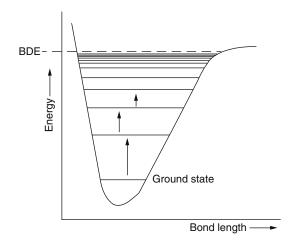
A plot of potential energy vs. interatomic distance, sometimes called a Morse curve [B], will look like Figure 7.1.

The lowest energy state, the ground state, is not exactly at the bottom of the "potential well." The point at the very bottom is the zero-point energy, which is the energy the bond would retain at absolute zero to avoid disobeying the Heisenberg Uncertainty Principle [C]. Addition of energy to the bond, usually thermal energy, promotes the system to a higher state of vibrational energy, see Figure 7.2.

Further additions of energy promote the system to higher and higher vibrational energy states until a state is reached at which the vibrational energy is the same as the energy of the two atoms separated to an "infinite" distance. At that point, there is no energetic benefit to having the two atoms in the bond, so they separate. The value of the energy at this point is known as the bond dissociation energy, BDE. A continuum of energy states lies above this value of bond dissociation energy. Every covalent chemical bond has a characteristic bond dissociation energy. A generic covalent chemical bond, A:B, can break in two ways. In homolytic cleavage, one electron from the electron pair in the bond goes with each fragment:



**Figure 7.1** The potential energy curve, or Morse curve, showing energy as a function of internuclear distance for a hypothetical molecule. The horizontal line depicts the vibrational energy ground state.



**Figure 7.2** Energy added to the system, e.g. as thermal energy, promotes a bond to successively higher vibrational states, until eventually an energy is reached that is equivalent to that of the atoms being separated to an infinite distance.

$$A: B \to A \bullet + \bullet B$$
,

whereas in heterolytic cleavage the electron pair stays with one of the fragments:

$$A: B \rightarrow A^+ + : B^-.$$

Whether a given bond in a molecule will undergo homolytic or heterolytic cleavage depends on the reaction conditions and whatever reagents (if any) with which the molecule

might be reacting. Homolytic bond cleavage processes in fuel chemistry can be initiated most commonly by heat or by reaction with reagents that are themselves radicals. Though much less common in fuel chemistry, homolytic cleavage can also be initiated by irradiation with light (photolysis), or with X-rays,  $\gamma$ -rays, or electron beams (radiolysis). Heterolytic reactions can be accelerated by acid or base catalysis, though radical reactions are not. Heterolytic reactions are not affected by light. Polar effects, such as sensitivity to solvent polarity, are much less for radical reactions than for corresponding ionic reactions.

# 7.2 Radicals

In the literature of the nineteenth century and early decades of the twentieth, the term *radical* referred to a specific part of a molecule; as an example, it might be said that the xylene molecule,  $C_6H_4(CH_3)_2$ , contains two methyl radicals. In that era, the adjective free was used to differentiate species that exist as separate entities, such as a methyl free radical,  $CH_3^{\bullet}$ , from the names that referred to part of a molecule. Nowadays the term *group* is used to designate part of a molecule, e.g. two methyl groups in xylene. Thus the adjective *free*, though often still used, is not, strictly speaking, necessary.

## 7.2.1 Initiation reactions

In thermally induced (i.e. non-catalytic) bond cleavage of hydrocarbon molecules, homolytic bond cleavage dominates. The products are radicals. Three features characterize radicals: at least one unpaired electron in the molecule, electrical neutrality, and, usually, high reactivity.

Combining two atoms to form a covalent bond releases energy, i.e. the enthalpy of the new product molecule is lower than that of the separate atoms. An example is combination of two hydrogen atoms to form a diatomic hydrogen molecule,  $H_2$ . This strongly exothermic reaction has an enthalpy change of -435 kJ/mol. As a consequence, bond-breaking reactions are always endothermic; energy has to be supplied to break a covalent bond. The amount of energy required, the homolytic bond dissociation energy, is exactly equal to the energy released when the separated atoms combined to form the bond. Table 7.1 provides values for the dissociation energies for some bonds

Bond	Energy	Bond	Energy	
H–H	435	CH <sub>3</sub> -CH <sub>3</sub>	368	
CH <sub>3</sub> -H	435	CH <sub>3</sub> CH <sub>2</sub> -CH <sub>3</sub>	356	
CH <sub>3</sub> CH <sub>2</sub> -H	410	CH <sub>3</sub> CH <sub>2</sub> -CH <sub>2</sub> CH <sub>3</sub>	343	
$(CH_3)_2CH-H$	395	(CH <sub>3</sub> ) <sub>2</sub> CH–CH <sub>3</sub>	351	
(CH <sub>3</sub> ) <sub>3</sub> C–H	381	(CH <sub>3</sub> ) <sub>3</sub> C–CH <sub>3</sub>	335	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -H	356	CH <sub>3</sub> –OH	383	
CH <sub>2</sub> =CHCH <sub>2</sub> -H	356	CH <sub>3</sub> O–CH <sub>3</sub>	335	
CH <sub>2</sub> =CH-H	452	HO–H	498	
C <sub>6</sub> H <sub>5</sub> -H	460	CH <sub>3</sub> CH <sub>2</sub> O–H	431	

Table 7.1 Homolytic bond dissociation energies, kJ/mol, at  $25 \degree C$  [1]. The bond being broken is shown with an em dash.

of interest in fuel chemistry; these values refer only to homolytic bond cleavage. The actual dissociation energy of any bond depends on its chemical environment in the molecule in which it occurs. Consequently, the value for any given type of bond, e.g. C–H, changes slightly from one species to another, to reflect structural differences between the species.

In most reactions of interest in fuel chemistry, the energy needed to drive homolytic bond cleavage is provided by heat, i.e. these are pyrolytic processes.

Among alkanes, the relative ease of homolytic C–C bond cleavage increases with increasing molecular weight. Decane, hexadecane, and dotriacontane ( $C_{32}H_{66}$ ) display relative reactivities for C–C bond breaking of 1:1.85:3 at 425°C. This behavior has importance in the pyrolytic processing of petroleum fractions (Chapter 16), because the higher-boiling fractions contain the larger alkanes, which are relatively easier to break apart – crack – than smaller compounds in the lower-boiling fractions.

In fuel chemistry many of the compounds that we deal with contain several kinds of bond, and often we deal with mixtures of many different compounds. At temperatures high enough to drive pyrolysis of any one kind of bond, often other kinds of bond break as well. Further, the immediate products of pyrolysis may undergo one or more subsequent reactions (as described below). As a result, pyrolysis processes usually give complex mixtures of products. They have little utility if the intent is to produce a single product in high yield.

A second route to formation of radicals is the reaction of a stable molecule with an already existing radical, e.g.

$$A: B + X \bullet \to A: X + B \bullet.$$

If a radical reacts with a molecule that is not also a radical (i.e. with a molecule in which all electron spins are paired), at least one product must still be a radical. Such reactions fall into two categories: those in which a radical abstracts an atom (very often a hydrogen atom) from a neutral molecule; or those in which a radical adds to a double bond. In either case, the radicals are able to enter into other reactions, often a sequence of reactions, as described below. Because reactions that produce radicals from existing stable molecules often begin a series of follow-on reactions, the radical-producing reactions are called initiation reactions.

Values of homolytic bond dissociation energies provide the way to estimate the relative stabilities of radicals. The more energy that must be supplied to produce a radical, the more that has been absorbed by the radical, and hence the greater its potential energy. Stability relates inversely to potential energy; hence a secondary radical is more stable than a primary radical because it requires less energy to produce. (The stability of radicals refers to stability relative to the hydrocarbon from which they were formed.) The same argument applies by extension to production of tertiary, methyl, and other types of radical. The more stable the radical, the more easily it is formed. The likelihood of homolytic cleavage of a given bond increases as the stability of the product radicals formed increases. Further, stability governs reactivity in a great many reactions involving radicals.

In methane, the four C–H bonds involve four  $sp^3$ -hybridized orbitals on the carbon atom. Radical formation changes the orbital hybridization to  $sp^2$  for the three remaining C–H bonds. This gives the radical a planar structure. The unpaired electron

91

occupies the unhybridized p orbital perpendicular to the plane of the three C–H bonds. The greater the number of alkyl groups involved in the tetrahedral-to-trigonal structural change, the more negative is the heat of formation.

In the ethyl radical, which can be thought of as derived from the methyl radical by replacing one of its hydrogen atoms with a  $-CH_3$  group, electron delocalization occurs by interaction of an electron pair in one of the  $sp^3$  orbitals of the  $-CH_3$  substituent with the partially filled *p* orbital on the carbon atom bearing the unpaired electron. This type of electronic interaction, called hyperconjugation, has a stabilizing effect on the radical. Increased opportunities for hyperconjugation in turn increase stability. The secondary isopropyl radical  $CH_3CH$ • $CH_3$  could be regarded as a methyl radical in which two hydrogen atoms are replaced by  $-CH_3$  substituents. The effect is further pronounced in the *tert*-butyl radical,  $(CH_3)_3C$ •. Hyperconjugative electronic interactions provide the basis of the stability that is observed in the sequence tertiary > secondary > primary > methyl.

# 7.2.2 Propagation reactions

Radicals, once formed, undergo a variety of reactions. Often, a radical reaction generates a new radical among the products. That new radical can, in turn, undergo similar reactions, some of which may have yet another, "third-generation" radical among their products. Radical reactions that generate new radicals are called propagation reactions, because they make it possible to continue a sequence of radical reactions. A sequence of such reactions is also known as a chain reaction, this term referring to any process in which a product of one step serves as a reactant in the next. Activation energies of propagation reactions are relatively low. If they were not, i.e. if there were some highenergy barriers in these reactions, reactive radicals would probably be consumed very rapidly in termination processes as discussed below, quickly bringing the sequence of reactions to a end.

Hydrogen abstraction reactions involve removal of a hydrogen atom from a molecule by a radical, e.g.

$$CH_3CH_2CH_3 + \bullet CH_3 \rightarrow CH_3CH \bullet CH_3 + CH_4.$$

This simple reaction of a methyl radical with propane also highlights the fact that hydrogen abstraction also depends on the position of the hydrogen atom in the molecule, i.e. whether it is a primary, secondary, or tertiary hydrogen. The analogous reaction with 2-methylpropane (isobutane) would be even faster:

$$(CH_3)_3CH + \bullet CH_3 \rightarrow (CH_3)_3C \bullet + CH_4$$

A hydrogen atom on a tertiary carbon atom is abstracted more rapidly than one on a secondary carbon atom, and this in turn more rapidly than a hydrogen atom on a primary carbon atom. This relative ranking of rate of hydrogen abstraction comes directly from the strengths of the relevant C–H bonds. The strength of the bond between the tertiary carbon atom in isobutane and the hydrogen atom attached to it is 385 kJ/mol. This value rises to 397 kJ/mol for a C–H bond on the secondary carbon atom in propane, and rises still further to 410 kJ/mol for a C–H bond in ethane.

Hydrogen abstraction make it possible to probe the relative stabilities of different kinds of radical. For an ethyl radical reacting in a mixture of ethane and methane two reactions might occur:

$$CH_3CH_2\bullet+CH_3CH_3\rightarrow CH_3CH_3+CH_3CH_2\bullet$$

or

$$CH_3CH_2 \bullet + CH_4 \rightarrow CH_3CH_3 + \bullet CH_3.$$

In fact, the first reaction occurs almost exclusively, indicating that the ethyl radical, a primary (1°) radical, is more stable than a methyl radical. Reactions like those discussed here, and many similar reactions that have been tested, establish an order of stability for free radicals:

benzyl 
$$\approx$$
 allyl  $> 3^{\circ} > 2^{\circ} > 1^{\circ} >$  methyl  $>$  vinyl  $\approx$  phenyl

Knowing this order of radical stability helps predict the course and outcome of radical reactions.

The newly formed radical produced from a hydrogen abstraction reaction can in turn participate in additional hydrogen abstraction reactions, or in other radical reactions discussed below.

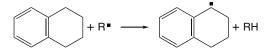
Hydrogen capping represents a special kind of hydrogen abstraction, with the hydrogen source deliberately provided as an external source of hydrogen. One such external source can be molecular hydrogen,  $H_2$ . Such a reaction can be represented as

$$R-CH_2 \bullet + H_2 \rightarrow R-CH_3 + H \bullet$$
,

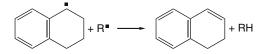
which might be followed by

$$R-CH_2 \bullet + H \bullet \rightarrow R - CH_3.$$

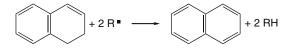
Alternatively, the H• could come from compounds called hydrogen donors, which contain one or more hydrogen atoms in positions from which they can easily be abstracted. The quintessential hydrogen-donor is 1,2,3,4-tetrahydronaphthalene, usually known by its trivial name, tetralin. Though numerous compounds are better hydrogen donors than tetralin, very many laboratory studies, especially in the field of direct coal liquefaction (Chapter 22) have used tetralin as a hydrogen donor. Loss of H• forms a benzyl radical:



Loss of a second H• produces 1,2-dihydronaphthalene:



The newly formed double bond conjugates with the aromatic ring. Loss of hydrogen atoms from the two remaining  $sp^3$  carbon atoms produces another benzyl radical and an allyl radical. Allylic and benzylic hydrogen atoms react readily in abstraction processes because removal of hydrogen from such positions produces a resonance-stabilized radical. Therefore these two remaining hydrogens are readily donated. The overall reaction is



Loss of the two remaining donatable hydrogen atoms from 1,2-dihydronaphthalene proceeds so readily that this compound can rarely, if ever, be isolated from reactions involving tetralin as a hydrogen donor.

 $\beta$ -Bond scission reactions contribute to breaking down, or fragmentation, of molecules. To illustrate  $\beta$ -bond scission with a 1° radical:

$$R-CH_2-CH_2-CH_2\bullet \rightarrow R-CH_2\bullet + CH_2 = CH_2.$$

The bond that breaks is  $\beta$  to the carbon bearing the radical. A 1° radical undergoes  $\beta$ -bond scission to produce ethylene and a new 1° radical that is shorter by two carbon atoms.  $\beta$ -Bond scission of a 2° radical tends to favor production of the radical product having the longer chain. For example, the reaction

# $$\label{eq:CH3} \begin{split} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 & \rightarrow CH_3CH_2CH_2CH_2CH_2\bullet\\ & + CH_2 = CHCH_2CH_2CH_3 \end{split}$$

is preferred instead of

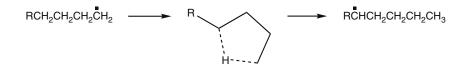
$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3} \rightarrow CH_{3}CH_{2}\bullet$$
$$+ CH_{2} = CHCH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}.$$

Exceptions occur when the opportunity exists to form an especially stable radical product, e.g. a new benzyl radical rather than a new 1° radical.

When  $\beta$ -bond scission of a 1° radical produces a new, shorter 1° radical plus ethylene, this process can continue, given appropriate reaction conditions, to form a second, even shorter 1° and more ethylene, and on and on... By selecting favorable reaction conditions – high temperatures to favor endothermic bond-breaking, and low pressures to favor gas formation – a large molecule, such as a hydrocarbon wax, can be converted to high yields of ethylene via consecutive  $\beta$ -bond scission reactions. This process, called wax cracking or "unzipping," has great commercial utility because ethylene is the world's most important industrial organic compound.

Reactive radicals will add to a wide variety of unsaturated compounds. The addition tends to attack at the least substituted position, controlled by the tendency to form the more stable radical intermediate.

An important distinction between radical reactions and reactions of carbocations to be discussed later is that alkyl radicals do not undergo rearrangements of the carbon structure. Some uncommon radicals undergo rearrangement, but such reactions are not of importance in fuel chemistry. However, long-chain 1° radicals can convert to a more stable 2° radical if the chain coils into a configuration that allows the 1° radical to abstract a hydrogen atom from one of the interior carbon atoms:



The carbon atom from which hydrogen is abstracted is usually four or five atoms back along the chain, so that the transition states involve five- or six-membered rings; the reactions are termed 1,4- or 1,5-hydrogen shifts, also sometimes called "back biting." The reactions illustrated here convert 1° to 2° radicals. With other structures, 3°, benzylic, or allylic radicals could be produced. Hydrogen shift reactions belong to the category of propagation reactions, because the product is a new radical.

A hydrogen shift over a distance greater than that from the 5- to the 1- position becomes less and less probable with increasing distance over which the atom must be moved. This is due to a steady decrease in likelihood of attaining a chain conformation that allows such a shift as chain length progressively increases. For shorter chain lengths, hydrogen shift becomes more and more difficult because attaining a co-linear arrangement that allows the hydrogen atom to move incurs greater strain as the chain length is reduced.

The only other type of rearrangement somewhat common in radicals is a 1,2-shift, which usually involves migration of aryl groups. Only rarely would an alkyl or cycloalkyl group move. These reactions take place when the rearrangement provides a radical more stable than the original one. As an example, when the 2,2,2-triphenyl-ethyl radical is stabilized, the dominant product is 1,1,2-triphenylethane.

### 7.2.3 Termination reactions

Radical reactions in which only one or more stable molecules are formed are referred to as termination reactions, because they bring a radical chain reaction to an end. For any further reaction to continue, a new initiation process would be required.

The most common termination process occurs when two radicals, which are not necessarily identical, combine, e.g.:

$$A \bullet + \bullet B \rightarrow A : B.$$

Such processes are called radical combination, radical recombination, or radical coupling reactions. These reactions have activation energies very close to zero, so the rate of diffusion of two radicals to get close enough to combine usually limits the rate of recombination. Rate constants for such reactions can be extremely high, of the order of  $10^{10} \text{ s}^{-1} \text{ mol}^{-1}$ . In the gas phase, the activation energy for radical combination reactions is zero, because the process is the reverse of homolytic cleavage of the bond being formed. Cases in which there is significant steric hindrance as the radicals come together would be exceptions. The heat of reaction is the reverse of the bond dissociation energy. In many cases in fuel chemistry, the recombination product is less reactive than were the molecules in the original feedstock. (Generally, the radicals are less stable than the products, and the reactions are not reversible.) In these cases, the feedstock is converted not to desired product, but to something else that is even harder to react. In these circumstances, radical recombination reactions are also known as retrogressive reactions, because the reaction is going in the wrong direction.

In many radical reactions, the radical concentration is less than the concentrations of other molecules. From the low concentration of radicals, it might seem that those products that clearly derive from radical combination reactions would form in lower concentrations than the many other kinds of product that could arise from reactions of radicals with non-radicals. In some cases, however, the recombination product turns out to be a sizeable fraction of the total products, because even though collisions between radicals might be rare, they are very effective when they do happen. A second factor that would suggest termination reactions to be rare is that the energy released when the new bond forms has to be dissipated if the two fragments are to stay together. Since the energy release on bond formation is essentially equal to the dissociation energy, if energy is not dissipated it could cause the bond to come apart again.

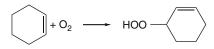
Disproportionation occurs when a hydrogen atom on a position  $\beta$  to the radical center moves from one radical to another. Disproportionation represents a special variant of hydrogen abstraction. In this case, a radical abstracts a hydrogen atom from another radical. The second radical is not necessarily identical with the first, but certainly can be. For example, two propyl radicals could react as

```
CH_3CH \bullet CH_3 + CH_3CH \bullet CH_3 \rightarrow CH_3CH_2CH_3 + CH_3CH = CH_2.
```

When the reacting radicals derive from saturated hydrocarbons, as in this example, the products are an alkane and the corresponding alkene. Both products are stable (i.e. non-radical) molecules that cannot propagate other radical processes. As with radical combination reactions, rates of disproportionation are very high, at least for simple alkyl radicals.

# 7.3 Radical reactions with oxygen

In air, many compounds undergo a slow oxidation process, autoxidation. Molecular oxygen is a diradical, readily reacting with radicals to form peroxides. Such reactions occur at or near ambient temperatures, much slower, and at much lower temperature, than combustion. Sunlight often serves as the initiator. Reactive radicals also serve as initiators. Autoxidation of unsaturated compounds occurs because of the easy abstraction of an allylic hydrogen atom. For example, cyclohexene reacts with atmospheric oxygen, in the presence of an initiator, to produce initially 3-cyclohexenyl hydroperoxide:



Subsequent reactions of the hydroperoxides lead to allylic radicals, which oligomerize to high molecular weight, highly viscous or hard materials. These processes are responsible for formation of gummy deposits when plant oils are used as diesel fuels (Chapter 5), hardening of exuded resins used by plants to seal wounds (Chapter 6), and formation of gums from alkenes in gasoline (Chapter 14) [D][E].

The first two steps in most oxidations are, in general,

$$C-H+O_2 \rightarrow C\bullet + H-O-O\bullet$$

and

$$C \bullet + O_2 \rightarrow C - O - O \bullet$$

Using isobutane as an example, the first step is abstraction of the tertiary hydrogen atom by an oxygen molecule:

$$(CH_3)_3CH + O_2 \rightarrow (CH_3)_3C^{\bullet} + \bullet OOH.$$

How readily H• can be removed by oxygen depends on the kinds of group attached to the carbon atom that will become the radical center. The *tert*-butyl radical formed in this step reacts with oxygen

$$(CH_3)_3C \bullet + O_2 \rightarrow (CH_3)_3COO \bullet.$$

Several possibilities exist for what might happen next.

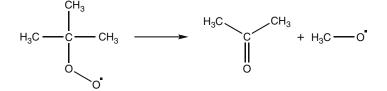
One possible reaction path would be formation of *tert*-butyl hydroperoxide,

$$(CH_3)_3COO\bullet + (CH_3)_3CH \rightarrow (CH_3)_3COO\bullet + (CH_3)_3C\bullet.$$

Alternatively, two tert-butyl peroxy radicals could eliminate oxygen,

$$(CH_3)_3COO \bullet + \bullet OOC(CH_3)_3 \rightarrow (CH_3)_3CO \bullet + O2 + \bullet OC(CH_3)_3$$

The former is the more likely. At higher temperatures, more typical of combustion processes than lower-temperature autoxidation, other reaction pathways could well occur. One such is a concerted reaction that breaks a C–C and an O–O bond simultaneously:



The propagation reactions

$$C \bullet + O_2 \rightarrow C - O - O \bullet \rightarrow C - OOH + C \bullet \rightarrow etc.$$

proceed readily. Reaction of ROO• radicals with C–H bonds proceeds more readily at  $2^{\circ}$  or  $3^{\circ}$  carbon atoms than at  $1^{\circ}$  atoms. Removal of hydrogen from an allylic or benzylic carbon atom is even easier. Every additional alkyl group on the radical center enhances removal of hydrogen by a factor of three; hydrogen-atom removal from benzylic carbon atoms is easier by a factor of about 25, and, from allylic carbon atoms, by a factor of about 100. This again illustrates the fact that molecules that form particularly stable radicals are the most reactive. Compounds with benzylic, allylic, or tertiary carbon atoms show the greatest susceptibility to oxidation. For any compound, however, the basic chain mechanism in autoxidation, beginning with the attack of some reactive radical (designated as In•) to initiate the process is

$$In^{\bullet} + R - H \rightarrow R^{\bullet} + In - H,$$
  

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet},$$
  

$$ROO^{\bullet} + R - H \rightarrow ROOH + R^{\bullet}.$$

For reactions that occur without added initiators, autoxidation of hydrocarbons can be autocatalytic. Hydroperoxides serve as excellent radical initiators. During the early stages of autoxidation the concentration of hydroperoxide is steadily increasing, i.e. more and more chains can be initiated by the hydroperoxide formed. Early in the process, the rate may be nearly proportional to the quantity of oxygen absorbed.

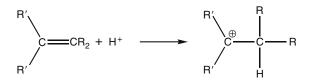
Autoxidation can be retarded or stopped altogether by adding antioxidants to the system. Some antioxidants react with peroxy radicals, preventing the chain reaction from occurring; others react with potential initiators, preventing initiation even from starting. So-called hindered phenols, in which the phenolic group is partially shielded by bulky alkyl groups, are widely used antioxidants, reacting with alkylperoxy radicals more readily than do alkanes. 2,6-Di-*tert*-butyl-4-methylphenol, usually known by its trivial name BHT (butylated hydroxyl toluene), provides an example, being widely used in plant oils, petroleum products, plastics and rubbers, and food. Rather than propagating a chain reaction, the radicals that result from reaction of the antioxidant terminate the chain, for example by dimerizing.

## 7.4 Carbocations

Heterolytic cleavage of a bond between a carbon atom and another atom can occur, in principle, in two ways:

$$\begin{split} \mathbf{C}\!:\!\mathbf{X} &\rightarrow \mathbf{C}^{+}\!+\!:\!\mathbf{X}^{-},\\ \mathbf{C}\!:\!\mathbf{X} &\rightarrow \mathbf{C}\!:^{-}+\mathbf{X}^{+}. \end{split}$$

The first reaction produces a positively charged, trivalent carbon cation, a carbocation. Both carbon radicals and carbocations are electron-deficient species; ordinarily, both are highly reactive, short-lived intermediates. The species  $C:^-$  is a carbanion, which is also highly reactive but which does not have much role in fuel chemistry. The process shown above represents one way of generating carbocations: direct ionization. Alternatively, a proton or other positively charged species can add to an alkene, or to an alkyne, also producing a carbocation.



Heterolytic bond dissociation energies are much higher than corresponding homolytic processes. As examples, which can be compared with the values in Table 7.1, heterolytic bond dissociation energies are 1678 kJ/mol for the H–H bond, 1310 kJ/mol for  $CH_3-H$ , and 1146 for  $CH_3-OH$ . The higher values for heterolytic processes derive from the additional energy needed to separate two electrically charged species, relative to separating neutral species. Producing carbocations by simple gas-phase reactions is, therefore, strongly endothermic. For example, the heat of formation of the *tert*-butyl carbocation,  $(CH_3)_3C^+$ , a particularly stable carbocation, is +678 kJ/mol.

The relative stabilities of carbocations follow the same order established for carbon free radicals: tertiary > secondary > primary > methyl. Alkyl groups tend to be electron-releasing groups, meaning that they will shift electron density

toward the site of positive charge, i.e. the positive charge becomes partially delocalized to the alkyl groups. Ethyl, isopropyl, and *tert*-butyl carbocations have, respectively, one, two, and three methyl groups contributing to their stability, thus the tertiary carbocation is the most stable; and the primary the least stable. An excellent rule of thumb is that the more stable the ion, the faster it is formed. Vinyl and phenyl carbocations are relatively unstable and not easy to form. In contrast, allyl and benzyl carbocations are particularly stable, because of the resonance delocalization of the positive charge in the allylic carbocation, and delocalization of the positive charge over the aromatic ring in the benzylic carbocation. Primary allylic or benzylic carbocations have about the same stability as secondary alkyl carbocations.

Differences in stability from one type of structure to another are more pronounced for the carbocations than for corresponding radicals. As examples, the *tert*-butyl radical is about 50 kJ/mol more stable than the methyl radical; but the difference between *tert*-butyl and methyl carbocations is about 300 kJ/mol.

The contribution of the alkyl groups to stability of carbocations is another manifestation of hyperconjugation. In the carbocation, the unhybridized p orbital is completely empty. Hyperconjugation involves electron donation from the alkyl substituent to the carbocation site, which is clearly electron-deficient. Hyperconjugation provides even greater stability to carbocations than to radicals.

An important property of carbocations, and one that we are at some pains to exploit in fuel chemistry, is their ability to undergo structural rearrangements of the carbon skeleton. As a rule, rearrangements are very fast, and are favored when the newly produced carbocation is more stable than the original. Carbocations can rearrange via a process known as a hydride transfer, or hydride shift, though the :H<sup>-</sup> ion does not appear to form; the reaction does, however, involve movement of hydrogen. A hydrogen atom interacts with the empty p orbital on the carbocation site. During the transition state, both carbon atoms that are involved rehybridize. The carbon atom that was an  $sp^2$ -hybridized site, i.e. the positive center of the carbocation, rehybridizes to  $sp^3$  as a bond forms between the carbon atom and the hydrogen atom that is migrating with its pair of electrons. At the same time, the carbon atom that was the site from which the hydrogen departed and was an  $sp^3$ -hybridized carbon rehybridizes to  $sp^2$  and acquires the positive charge. As an example:

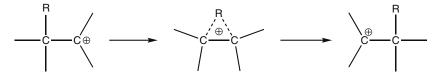
#### $(CH_3)_2CHCH^+CH_3 \rightarrow (CH_3)_2C^+CH_2CH_3.$

This process converts a secondary to a tertiary carbocation.

In the analogous process of alkyl group migration, the migrating alkyl group moves with its pair of electrons, forming, in this case, a new C–C bond with the carbocation center. The net effect is that the carbocation site and the alkyl group exchange places. As an example of this reaction:

$$(CH_3)_3CCH^+CH_3 \rightarrow (CH_3)_2C^+CH(CH_3)_2$$
.

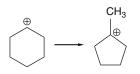
Again a secondary carbocation has rearranged to a more stable tertiary ion. Migration of the alkyl group occurs through a bridged intermediate or transition state that involves a three-center bond, using two electrons from the migrating group:



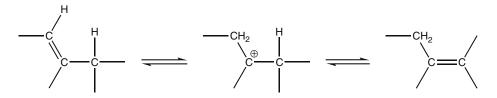
Regardless of whether the migrating group is a hydride or an alkyl group, it never completely leaves the molecule.

Activation energies for rearrangements tend to be small. Because of the thermodynamic driving force and the low activation barrier, rearrangements that convert carbocations to a more stable structure are virtually inevitable.

Most carbocation rearrangements involve a 1,2-shift of the migrating group, but rearrangements are not restricted to 1,2-shifts. Carbocationic ring contraction of cyclohexane to methylcyclopentane, important in processing of gasolines (Chapter 14), provides an example:



Another type of rearrangement involves migration of a double bond. This can occur readily by protonation of the double bond, followed by loss of a proton from another carbon atom:



Double-bond migrations within a carbon skeleton yield the most stable double bond isomer, i.e. the one in which the double bond is conjugated or most heavily substituted.

Carbocations undergo a variety of reactions in addition to the structural rearrangements just discussed. These reactions include a combination of the cation with a negative ion; abstraction of hydride from an alkane to form a new carbocation; loss of a proton to form an alkene; and addition to an alkene to produce a new, larger carbocation [F]. The first two reactions on this list can be considered the carbocationic analogs of the recombination and hydrogen abstraction reactions of radical chemistry. Reactions in which carbocations react to give stable products, such as combining with a negatively charged species possessing an electron pair, are very fast.

Addition of a carbocation to an alkene is important in gasoline production (Chapter 14). Reaction of isobutane with 2-methylpropene (isobutylene) provides an example. In the presence of an acidic catalyst, such as concentrated sulfuric or hydrofluoric acid, a proton adds to the double bond in isobutylene to produce the *tert*-butyl carbocation:

$$(CH_3)_2C=CH_2+H^+ \rightarrow (CH_3)_3C^+.$$

The *tert*-butyl carbocation adds to the double bond of another molecule of isobutylene, to produce an eight-carbon carbocation:

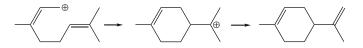
$$(CH_3)_2C=CH_2+(CH_3)_3C^+ \rightarrow (CH_3)_2C^+CH_2C(CH_3)_3$$

The new, larger carbocation then abstracts a hydride from a molecule of isobutane:

$$(CH_3)_2C^+CH_2C(CH_3)_3 + (CH_3)_3CH \rightarrow (CH_3)_2CHCH_2C(CH_3)_3 + (CH_3)_3C^+$$

This step produces a stable alkane of eight carbon atoms, and a new *tert*-butyl carbocation. As Chapter 14 discusses, the stable product of this reaction, 2,2,4-trimethylpentane, boils in the gasoline range, so its formation enhances the yield of gasoline. The product is also desirable because it has an octane rating of 100.

Carbocation addition to double bonds has a role in biosynthetic cyclization reactions that lead to naturally occurring compounds containing cycloalkane or cycloalkene ring systems. An example occurs in the formation of limonene, a pleasant-smelling component of oil of lemon:



The persistence of five- and six-membered ring structures from natural compounds through the various transformations to form fossil fuels may account for the presence of cycloalkanes in petroleum.

Many carbocation reactions, like the example above, generate new carbocations among the products. Just as in the case of radical reactions, these "second generation" carbocations participate further in various carbocation reactions, creating a chain of reactions that continues until it eventually terminates in formation only of stable, nonionic products. Hence initiation, propagation, and termination processes occur with carbocations just as with radicals.

## 7.5 Hydrogen redistribution

Many reactions throughout fuel chemistry involve, in some fashion, a reallocation of hydrogen among the products. Because of this, a way of keeping track of the hydrogen in the system, and where it goes, can be useful. Several methods can be used to do this. A convenient and useful hydrogen-bookkeeping tool is the atomic (not mass) H/C ratio. When molecular formulas are known, the atomic H/C ratio can be determined easily, often by inspection, or certainly by simple calculation. If analytical data are used, calculation of the atomic H/C ratio is also straightforward:

$$(\mathrm{H/C})_{\mathrm{atomic}} = (\mathrm{H/C})_{\mathrm{mass}} \cdot (12/1).$$

Two reactions of the propyl radical,  $\beta$ -bond scission and disproportionation, illustrate the redistribution of hydrogen in radical processes. The same approach applies to carbocation reactions,

$$CH_3 - CH_2 - CH_2 \bullet \rightarrow \bullet CH_3 + CH_2 = CH_2.$$

In this  $\beta$ -bond scission reaction, the propyl radical has an atomic H/C ratio of 2.33. In the products, the methyl radical has an H/C of 3.00 and ethylene, 2.00. For disproportionation,

$$CH_3 - CH_2 - CH_2 \bullet + CH_3 - CH_2 - CH_2 \bullet \rightarrow CH_3 - CH_2 - CH_3 + CH_2 = CH - CH_3$$
,

the propyl radical of H/C 2.33 forms propane, with an H/C ratio of 2.67, and propene (propylene), 2.00. Without belaboring the issue, the key conclusion is that, *in the absence of an external source of hydrogen*, reaction processes of hydrocarbons result in two kinds of product: those that are hydrogen-rich (i.e. higher H/C ratio) relative to the starting material, and those that are carbon-rich (i.e. lower H/C ratio). We explore the consequences of this in future chapters.

## Notes

- [A] For years a trivalent species with a positive charge on a carbon atom was called a carbonium ion, e.g. the methyl ion  $CH_3^+$ . This was a long-standing practice in organic nomenclature, despite the fact that the suffix-*onium* usually refers to a species having valence higher than that of its neutral atom, e.g. tetravalent nitrogen in the ammonium ion,  $NH_4^+$ . For decades, the term carbonium ion was used throughout the literature in reference to species such as  $CH_3^+$ . The American chemist George Olah (Nobel Prize, 1994) demonstrated the possibility of producing pentavalent carbon species, such as  $CH_5^+$ , in superacid media. These pentavalent species are true carbonium ions, whereas the term *carbocation* has come into general use for the trivalent positive species.
- [B] Named in honor of the American physicist Philip Morse (1903–1985). In his distinguished career, Morse served for a time as director of Brookhaven National Laboratory and was a founding director of the acoustics laboratory at the Massa-chusetts Institute of Technology. Morse is also recognized as one of the major figures in establishing the field of operations research.
- [C] If the vibrational ground state lay at the very bottom of the Morse curve, we could in principle specify exactly both the positions and velocities of the two atoms in the bond, violating the Uncertainty Principle.
- [D] These processes are also responsible for the way in which foods containing fats or oils with unsaturated fatty acid chains, such as butter, become rancid. In this case, autoxidation results in degradation of the long fatty acid chains to shorter carboxylic acids, many of which have very unappealing aromas and tastes.
- [E] Some plant oils, especially linseed oil and tung oil, have been used in paints, varnishes, and lacquers because of the hard, water- and air-tight coating produced by their autoxidation reaction. These oils react readily with oxygen because they contain, as triglycerides, fatty acids that contain two or more C=C bonds. Hydrogen atoms  $\alpha$  to the C=C bonds in these acids are easily abstracted by oxygen, a process that induces a radical polymerization of the oil.
- [F] Carbocations also can alkylate aromatic rings. This is not of much interest in fuel chemistry, where often we would rather carry out dealkylation. However, the reaction has great importance in the related field of petrochemicals, where alkylation of benzene with ethylene is the first step in the route to production of

polystyrene (via ethylbenzene and its dehydrogenation to styrene). Alkylation of aromatic rings is also of great interest in organic synthesis, exemplified by the Friedel–Crafts reaction, discussed in some detail in most introductory organic chemistry texts.

#### Reference

[1] Adapted from Solomons, T.W.G. Organic Chemistry, Wiley: New York, 1988; p. 400.

#### **Recommended reading**

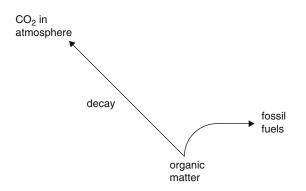
- Carey, Francis A. and Sundberg, Richard J. Advanced Organic Chemistry. Part A. Structure and Mechanisms. Plenum Press: New York, 1990. Chapter 12 provides an extensive review of radical reactions, while Chapters 5 and 6 discuss many aspects of carbocation chemistry.
- Fossey, J., Lefort, D., and Sorba, J. *Free Radicals in Organic Chemistry*. Wiley: Chichester, 1995. A first-rate introduction to radical processes, going much deeper than this chapter and any of the introductory texts in organic chemistry.
- Isaacs, Neil S. *Physical Organic Chemistry*. Longman Scientific and Technical: Harlow, UK, 1987. Chapter 15 provides a solid discussion of radical reactions.
- Morrison, Robert T. and Boyd, Robert N. Organic Chemistry. Prentice Hall: Englewood Cliffs, NJ, 1992. All modern introductory textbooks of organic chemistry provide discussions of carbocations and their reactions. This book is particularly useful.
- Pine, Stanley H. *Organic Chemistry*. McGraw-Hill: New York, 1987. Chapter 24 provides a good review of free radicals and their reactions. The discussion includes many kinds of compound not treated here, including halogenated and other heteroatomic compounds.
- Smith, Michael B. and March, Jerry. March's Advanced Organic Chemistry. Wiley: Hoboken, NJ, 2007. Chapter 5 is an excellent overview of the reactive intermediates of organic chemistry, with much useful information on radicals and carbocations.
- Stein, S.E. A fundamental chemical kinetics approach to coal conversion. In: New Approaches in Coal Chemistry. (Blaustein, B.D., Bockrath, B.C., and Friedman, S., eds.) American Chemical Society: Washington, 1981; Chapter 7. A useful and detailed review of radical chemistry. Though the emphasis is on coal chemistry, the material in this chapter has wide applicability throughout much of fuel chemistry.

While ethanol, biodiesel, and wood show greater or lesser success in meeting the ideals of renewability and  $CO_2$  neutrality, there also remain questions: the availability of enough arable or forested land to meet energy demand through biomass; availability of adequate water supplies for biomass growth; and, for ethanol and some biodiesel sources, the continuing argument of food vs. fuel. Consequently, most industrialized nations continue to rely heavily on fossil fuels to meet their energy needs. Fossil fuels will be vital contributors to world energy needs for many decades to come.

Chapter 1 introduced the global carbon cycle, shown as in Figures 1.1 and 1.5. The origin of fossil fuels represents a "detour" on the right hand side of the global carbon cycle, as shown in Figure 8.1.

Though the sequence of reactions or transformations of organic matter to fossil fuels is complicated, the same reasoning applies as would be used in studying simpler reactions in the laboratory. The important information includes the nature of the starting materials, reaction conditions (temperature, pressure, time, and catalysis), and some knowledge of reaction mechanisms.

Formation of fossil fuels from organic matter results from the fact that decay of organic matter "only" goes 98–99% to completion. A fossil is a remnant of a onceliving organism now preserved in Earth's crust. Our use of the term *fossil fuels* implies that these fuels derive from the chemical components of living organisms. Several lines of evidence support this [A]. Both petroleum and coal contain compounds, called biomarkers, known to occur in living organisms, or that clearly derive from compounds of biological origin. An example is 2,6,10,14-tetramethylpentadecane (pristane), found



**Figure 8.1** A tiny portion of the global carbon cycle, reduced from Figure 1.4, showing that fossil fuel formation represents an alternative reaction pathway for conversion of organic matter.

as a minor constituent of many petroleum samples and known to occur in waxes of living plants. Petroleum also contains compounds that are optically active, indicating the existence of chirality (i.e. structures not superimposable on their mirror images) in the molecule. Though chiral molecules can be synthesized from achiral starting materials, normally the occurrence of large quantities of chiral molecules in nature indicates their origin from other chiral molecules in biochemical processes. Coals provide even more direct evidence: the clear visual observation of coalified plant parts (Chapter 17).

The enormous amounts of fossil fuel still remaining on Earth represent the remnant of truly colossal quantities of organic matter. On average, some 7 kg of carbon accumulated in organic matter eventually resulted in 1 gram of carbon in fossil fuels. The world's annual fossil fuel consumption in 2005, equivalent to 7.5 gigatonnes of carbon, derived from about 50 teratonnes  $(50 \times 10^{12} \text{ tonnes!})$  of carbon in organic matter [1]. Environments favoring the extensive growth of living organisms share three characteristics: abundant light, moisture, and warmth. The precursors to fossil fuels accumulated in tropical or subtropical ecosystems [B] such as swamps, marshes, river deltas, and lagoons.

# 8.1 Diagenesis: from organic matter to kerogen

Chapter 1 introduced the decay process for a simple monosaccharide as

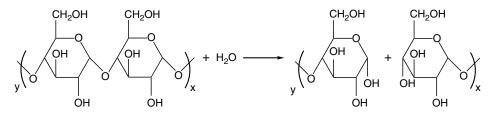
$$C_6H_{12}O_6 + 6O_2 \to 6\,CO_2 + 6\,H_2O.$$

Analogous reactions could be written for any of the other components of organic matter. The key reactant in decay is oxygen (from air). Most of the decay reactions experienced by accumulated organic matter are facilitated by enzymes in aerobic bacteria. These bacteria exist in extraordinary quantities, some  $10^9$  bacteria per gram of soil, and 3 tonnes of bacteria per hectare. Aerobic decomposition proceeds effectively at oxygen concentrations above 1 mg/l. Fossil fuel formation requires, as a first step, that the accumulated organic matter be preserved against the ravages of air, or by extension, against the action of aerobic bacteria. Covering organic matter with water that contains no dissolved oxygen – i.e. stagnant water – or with sediments such as mud or silt provides an effective way of doing this. During approximately the first meter of burial, oxygen can diffuse through the water or sediment in sufficient concentration to maintain the decay processes. Fossil fuel formation can be thought of as a race between the rate of decay, and the rate of burial, of organic matter.

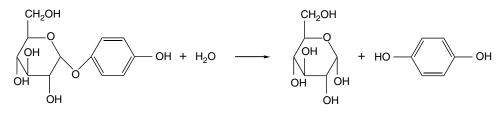
Below about 1 m, the oxygen content is depleted to a level at which aerobic decay stops. New chemical processes begin. These processes are also facilitated by bacteria, but by those that do not require molecular oxygen, i.e. anaerobic bacteria. The oxygen concentration in anaerobic conditions is typically less than 0.1 mg/l. Anaerobic bacteria can utilize sulfates or nitrates as energy sources, reducing them to hydrogen sulfide and nitrogen.

Reactants for anaerobic reactions come from the components of organic matter introduced in the previous chapters: cellulose and hemicellulose, starch, glycosides, lignin, proteins, fats and oils, waxes, steroids, resins, and hydrocarbons. Organic matter preserved at depths below 1 m represents a very rich chemical "stew." Molecules begin to break apart, generally by hydrolysis reactions. The temperature just a few meters into the Earth is very close to ambient, so the possibility of pyrolysis does not yet come into play. Pressure is also near-ambient.

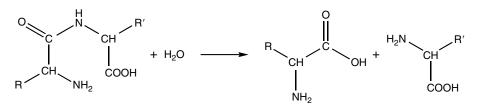
Under these conditions polysaccharides hydrolyze fairly easily:



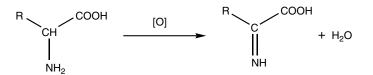
Similarly, glycosides react readily:



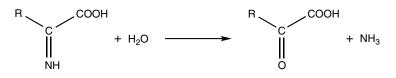
The peptide linkage is also susceptible to hydrolysis, e.g.:



Enzymes in anaerobic bacteria greatly accelerate these processes, by factors up to  $10^{10}$  for polypeptide hydrolysis. Though anaerobic bacteria do not utilize oxygen from air to drive their internal biochemical processes, still they must conduct oxidation processes somehow. Oxidative deamination of amino acids provides a route for accomplishing this, e.g.:



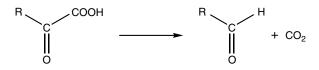
The product of this reaction, an imino acid, reacts with water to give ammonia and an  $\alpha$ -keto acid:



Functional group	Reactivity	Primary products	Secondary product
Saccharide	high	sugars	
Glycoside	high	sugars phenols	$CO_2 + CH_4$
Peptide	high	amino acids	$CO_2 + NH_3 + aldehydes$
Esters	moderate	fatty acids	
Waxes	low	fatty acids long-chain alcohols	
Ethers	very low	phenols	
Hydrocarbons	none	none	

Table 8.1 Hydrolytic reactivity and expected products from the principal constituents of organic matter.

This reaction accounts for the noticeable odor of ammonia in places where "organic matter" can accumulate in large and sometimes noxious quantities, such as stables and outdoor toilets. Chapter 4 introduced the characteristic decarboxylation reaction of  $\alpha$ -keto acids:



Anaerobic bacteria also attack monosaccharides, e.g.:

$$C_6H_{12}O_6 \rightarrow 3\,CH_4 + 3\,CO_2.$$

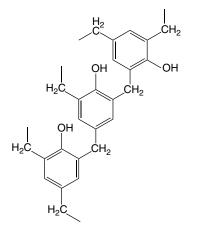
The important contrast with aerobic decay is that anaerobic reaction involves no molecular oxygen. Methane produced in this way has the trivial name marsh gas [C, D], sometimes also called biogenic methane, to distinguish its origin from that of methane produced later in the fuel formation processes.

Fats and oils do not hydrolyze extensively under these conditions. Ester groups in waxes are virtually impossible to hydrolyze under mild reaction conditions, in part because the functional group is deep inside a structure formed by two long, hydrophobic hydrocarbon chains. (In fact, we use waxes to provide a waterproof coating for wood and other materials.) Methoxy and other ether linkages in lignin do not react to any extent. Other components of organic matter, such as resins and the alkanes, lack hydrolyzable functional groups. Table 8.1 summarizes the expected hydrolytic reactions of organic matter.

As anaerobic reactions proceed, monosaccharides, amino acids, phenols, and aldehydes recombine to produce fulvic acids. These compounds, of ill-defined structure, have molecular weights in the range 700–10 000 Da, and dissolve in aqueous acid. Further condensation reactions lead to humic acids. Humic acids, brown to black, high molecular weight solids ( $\approx 10\,000-300\,000$  Da), dissolve in aqueous base but precipitate when the solution is acidified. This description of humic acids represents an operational definition: it does not really say what humic acids are; it only tells how they behave under certain conditions. Operational definitions will be encountered numerous times again, especially in discussions of petroleum and coal chemistry.

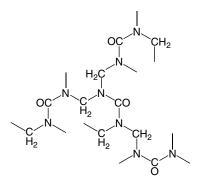
At a depth of about ten meters, action of anaerobic bacteria ceases. By this time the bacteria have consumed most of the material that they are capable of metabolizing. The phenolic compounds produced in some of the reactions function as bactericides [E].

Further, some bacteria, the actinomycetes, produce a variety of antibiotic compounds, including such medicinally important products as actinomycin, streptomycin, and tetracycline. The chemical mixture at this depth includes: humic acids; unreacted or partially reacted fats, oils, and waxes; slightly modified lignin; and resins and other hydrocarbons. These substances combine in poorly understood ways to form kerogen. Conceptual models of the structural arrangements in kerogen resemble phenol-formal-dehyde resins (8.1).



8.1 Phenol-formaldehyde resin

This is produced, in this example, from the reaction of phenol with formaldehyde. Urea-formaldehyde resins (8.2) provide another conceptual model.



8.2 Urea - formaldehyde resin

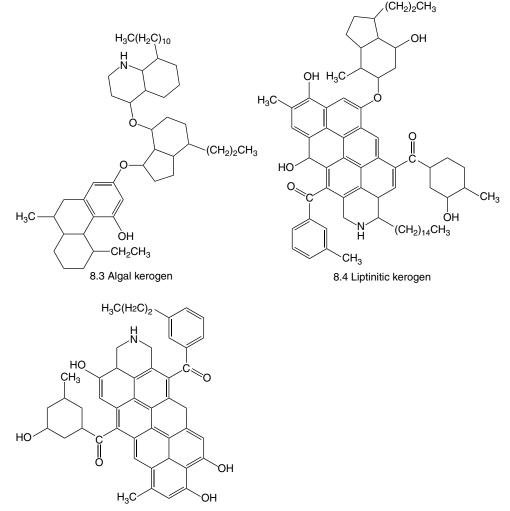
In nature, the reaction mixture would include many phenol derivatives, various aliphatic aldehydes, and various amines, not just phenol, formaldehyde, and urea. The resulting structures would become very complex, very rapidly.

Kerogen is operationally defined as a brownish-black, high molecular weight, polymeric organic solid insoluble in aqueous base, in non-oxidizing acids, and in common organic solvents. Three types of kerogen are recognized, depending on the dominant source of the organic matter (Table 8.2).

Representations of possible molecular structures of these kerogens are shown as 8.3, 8.4, and 8.5, for algal, liptinitic, and humic kerogens, respectively [2].

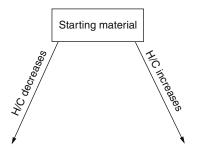
Source	Name	Туре
Algae	algal	Ι
Plankton	liptinitic	II
Woody plants	humic	III

Table 8.2 The types of kerogen, defined by the dominant source of organic matter.



8.5 Humic kerogen

Kerogen formation continues to a depth of about 1000 m, where temperatures might reach  $\approx$ 50 °C. Essentially, kerogen represents the "halfway point" between organic matter and fossil fuels. Because of the important role played by anaerobic bacteria, formation of kerogen is sometimes called the biochemical phase of fossil fuel formation.



**Figure 8.2** In any fuel chemistry system for which there is no external source of hydrogen, reactions proceed with the formation of one set of products more hydrogen-rich than the reactant(s), i.e. having higher atomic H/C ratio; and with formation of a second set of products more carbon-rich than the reactants, having lower atomic H/C ratio.

It is also called diagenesis, a word that means a transformation of materials by dissolution and recombination of their constituents. Formation of kerogen brings to a close the first phase of fossil fuel formation.

## 8.2 Catagenesis: from kerogen to fossil fuels

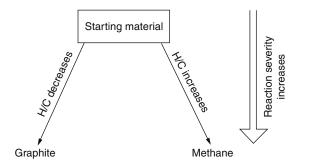
At the end of diagenesis, kerogen could be exposed to aerobic conditions, in which case it would gradually oxidize and be lost; or it could be buried increasingly deeply inside the Earth's crust, experiencing conditions that allow it to transform slowly into fossil fuels. Transformation of kerogen to fossil fuels is driven primarily by temperature – the natural heat in the Earth's crust. For this reason, transformation of kerogen is sometimes called the geochemical phase of fossil fuel formation. It is also called catagenesis, a word developed in the field of petroleum geology to describe the overall process of conversion of kerogen to hydrocarbon products. The heat derives mainly from the decomposition of radioactive materials, particularly  $^{40}$ K,  $^{232}$ Th,  $^{235}$ U, and  $^{238}$ U, in the crust. The geothermal gradient varies, depending on locality, but is typically 10–30 °C/km. Sometimes an unusual event, such as the intrusion of magma, might create a much greater amount of heating in a small area.

Reaction conditions in catagenesis range from about 60 to several hundred degrees, Pressures can be elevated because of the weight of overlying rocks, or, in some cases, by pressures caused by folding of rocks during mountain-building. Reaction times are very long, from thousands to millions of years. There are no externally supplied reactants, so the reactions that take place in catagenesis represent the structural or compositional rearrangement of the components of kerogen. These alterations are primarily driven by temperature.

Since catagenesis is driven by heat, we should expect that radical chemistry dominates. As introduced at the end of Chapter 7, radical processes occurring in the absence of external sources of hydrogen result in two kinds of product: those that are hydrogenrich (i.e. of higher H/C) relative to the starting material, and those that are carbon-rich (lower H/C). This rule holds all the way from a very simple species such as the propyl radical to a complex, macromolecular, ill-defined substance such as kerogen. An "inverted-V" diagram illustrates this (Figure 8.2).

Starting material	Molecular formula	Atomic H/C	Expected CH <sub>4</sub> /graphite ratio
Propane	$C_3H_8$	2.67	2.00
Heptane	$C_{7}H_{16}$	2.28	1.33
Heneicosane	$C_{21}H_{44}$	2.09	1.10
Toluene	$C_7H_8$	1.14	0.40
Chrysene	$C_{18}H_{12}$	0.67	0.20

**Table 8.3** A decrease in the atomic H/C ratio of the starting material is accompanied by a decrease in the relative amounts of hydrogen-rich to carbon-rich products, as indicated by a decrease in the methane-to-graphite ratio that would be observed upon complete catagenesis.



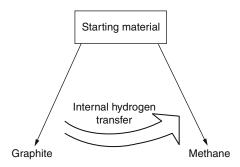
**Figure 8.3** Progression to hydrogen-rich and carbon-rich products in principle would lead to formation of methane and graphite, respectively. How far the system progresses toward these ultimate products depends on the severity of reaction conditions – temperature, time, pressure, and possibly catalysis.

To expand upon Figure 8.2, we can ask where the arrows go; in other words, what are the ultimate end points of catagenesis, see Table 8.3. The most hydrogen-rich carbon compound possible is methane,  $CH_4$ . It is also the most stable thermodynamically of the hydrocarbons. The ultimate carbon-rich material is carbon itself, i.e. H/C of 0. Graphite is the thermodynamically stable form of pure carbon.

Catagenesis of kerogen normally proceeds only part way to graphite and methane. As in any other chemical process, severity of reaction conditions determines the extent of reaction, i.e. how far kerogen transforms toward the ultimate products of graphite and methane. In catagenesis, time and temperature are the dominant conditions. This can be represented conceptually as shown in Figure 8.3.

In natural systems, the only way for the hydrogen-rich products to continue to increase the H/C ratio is by utilizing hydrogen pulled out of the carbon-rich products. This process accounts for the observed decrease in H/C ratio on the carbon-rich side. As catagenesis proceeds, hydrogen moves from the products of low H/C to those with high H/C, a geochemical manifestation of the saying that "the rich get richer and the poor get poorer." Figure 8.4 illustrates this.

The issue of which products – the H-rich or the C-rich – dominate must also be considered. As in other, simpler, chemical processes, stoichiometry of the reactants governs the outcome. If the original kerogen is relatively H-rich, the H-rich products dominate. Similarly, a kerogen relatively C-rich (or H-poor) gives predominantly



**Figure 8.4** Formation of the two sets of products, i.e. hydrogen-rich and carbon-rich, results from an internal transfer of hydrogen from the carbon-rich side to the hydrogen-rich.

carbon-rich products. The hypothetical transformation of simple compounds to methane and graphite illustrates the effect of the H/C ratio on the distribution of products. Toluene has an H/C ratio of 1.1. In the reaction

$$C_6H_5CH_3 \rightarrow 2CH_4 + 5C$$

the methane-to-graphite ratio would be 2:5, or 0.4. In comparison, heptane,  $C_7H_{16}$ , with the same number of carbon atoms as toluene, has an H/C ratio of 2.3. The comparable reaction gives

$$C_7H_{16} \rightarrow 4CH_4 + 3C$$
,

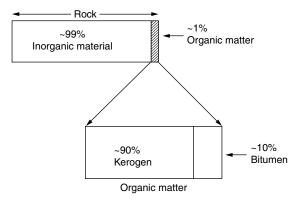
with a methane-to-graphite ratio of 4:3 or 1.33. The higher H/C ratio starting material gives a greater amount of H-rich products.

The three types of kerogen (Table 8.2) differ in H/C ratio. Types I and II (i.e. algal and liptinitic kerogens) have relatively high H/C ratios, about 1.7 and 1.4, respectively. In contrast, Type III, humic kerogen, has a relatively low H/C ratio, typically <1. Thus, it can be expected that Types I and II kerogens will give relatively H-rich products, whereas Type III will give relatively C-rich products. The principal H-rich products are petroleum and natural gas; the C-rich products, coals.

#### 8.3 Catagenesis of algal and liptinitic kerogens

High H/C and low O/C ratios characterize the elemental composition of lipid-rich Types I and II kerogens. Sedimentary deposits containing kerogen that transforms to petroleum and/or natural gas are called source rocks. The quality of a source rock depends on the amount of organic carbon it contains. To be considered a good source rock, the organic carbon content would be 1-2%; excellent, >4%. A portion of the organic carbon, roughly 10%, dissolves in common organic solvents such as chloroform or carbon disulfide. This material is bitumen. The insoluble remainder is kerogen. This is shown schematically in Figure 8.5.

The relationship between molecular size and physical properties is explored in more detail in Chapter 9, but as a good rule-of-thumb, formation of liquid products, and then gases, requires progressive degradation in molecular size. This can only be



**Figure 8.5** Many oil source rocks consist of approximately one percent of organic carbonaceous material, the rest being inorganic. Of the organic material itself, about 90% is kerogen and 10% bitumen.

accomplished by breaking C–C bonds. The key process for accomplishing reduction in molecular size is bond homolysis. Bond homolysis driven by temperature is sometimes called thermal cracking.

Petroleum contains thousands of individual compounds. Part of this complexity arises from the fact that thermal cracking reactions can give rise to a very large number of possible products. This is true even of the cracking of rather simple molecules such as butane. For example, the initial cracking of butane can proceed in two ways:

$$\begin{split} \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_3 &\to \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2 \bullet + \bullet\mathrm{CH}_3, \\ \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_3 &\to \mathrm{CH}_3\mathrm{CH}_2 \bullet + \bullet\mathrm{CH}_2\mathrm{CH}_3. \end{split}$$

The bond dissociation energies favor the latter reaction (343 kJ/mol for breaking the  $CH_3CH_2 - CH_2CH_3$  bond, vs. 364 kJ/mol for the  $CH_3CH_2CH_2 - CH_3$  bond), but both probably contribute in thermal cracking processes. C–C bond homolysis in butane gives rise to three radicals: methyl, ethyl, and propyl. Each of these radicals then undergoes one or more of the various free-radical processes introduced in Chapter 7. The possible outcomes are summarized in Table 8.4.

This example did not consider products larger than the original starting material, e.g. pentane from the combination of ethyl and propyl radicals. Even so, the relatively simple single compound butane gives rise to five stable reaction products: methane, ethane, ethylene, propane, and propylene.

But the molecules in bitumen or kerogen are much larger than butane, more like triacontane,  $C_{30}H_{62}$ . Initial C–C bond cleavage in triacontane can result in 29 different radicals, ranging from methyl to the nonacosyl primary radical,  $\cdot C_{29}H_{59}$ . Each can potentially undergo all of the radical processes discussed in Chapter 7. And, for each of the propagation reactions, the so-called second generation radicals can, and will, themselves undergo further reactions. The third, fourth... generation radicals will also react, until finally terminations result in an assemblage of stable products. The number of stable products from a single, large hydrocarbon exemplified by triacontane can be very great. Based on the example of butane generating all the possible smaller alkanes and alkenes, 57 alkanes and 1-alkenes could form.

Initial radical	Process	<b>Product</b> (s)	
Methyl	Hydrogen abstraction	Methane	
-	Recombination with $\cdot CH_3$	Ethane	
	Recombination with $\cdot CH_2CH_3$	Propane	
Ethyl	Hydrogen abstraction	Ethane	
•	Disproportionation	Ethane and ethylene	
	Recombination with $\cdot CH_3$	Propane	
Propyl	Hydrogen abstraction	Propane	
	Disproportionation	Propane and propylene	
	β-bond scission	Ethylene and $\cdot CH_3$	
	Cracking	•CH <sub>3</sub> and •CH <sub>2</sub> CH <sub>2</sub> •	

Table 8.4 Possible reaction products of the radicals produced during thermal cracking of butane.

Further complication comes from the fact that naturally occurring bitumen or kerogen does not consist of a single pure compound, but rather a mixture of many compounds, representing many possible molecular structures. In natural materials branched-chain structures, such as pristane, and cyclic structures, such as abietic acid, also occur. Thermal cracking in nature begins with a mixture of compounds containing roughly 16 to over 40 carbon atoms in linear, branched, and cyclic structures. Once cracking has started, all of the radical reactions discussed in Chapter 7 can, in principle, come into play. The liquid product that eventually forms from all of these reactions – petroleum – occurs as a mixture of the hundreds of possible products that arise from the application of a half-dozen types of radical reaction applied to these starting materials.

Conversion of kerogen to bitumen begins at approximately 60 °C. As thermal cracking begins, one might expect any C–C bond in a given molecule to break. Triacontane has two terminal C–C bonds that can break to give  $\cdot$ CH<sub>3</sub> and  $\cdot$ C<sub>29</sub>H<sub>59</sub>, but has 27 C–C bonds in the interior of the molecule. There is a greater likelihood that the molecule will crack somewhere in the interior rather than at one of the terminal C–C bonds. Consequently, the initial cracking products are more likely to be medium- to large-sized molecules.

As temperature increases, the rate of cracking also increases. Writing the Arrhenius equation in its expanded form:

$$\ln k = \ln A - E_a / RT$$

where k is the rate constant, A the pre-exponential factor,  $E_a$  the activation energy, R the gas constant and T the temperature in kelvin, indicates that oil formation increases linearly with time but exponentially with temperature. More C–C bonds are broken with increasing temperature. If the starting materials have come, in part, from earlier cracking reactions, they will be of still smaller molecular size. Not only will more bonds be broken, but the size of the product molecules will be smaller.

The first significant amounts of small hydrocarbons that would be gases at ambient conditions begin to appear around 110°C. By the time the temperature has reached  $\approx$ 170°C such extensive cracking has occurred that formation of the liquid product, petroleum, has ceased and now only gases form. The ultimate gaseous product of this extensive catagenesis would be methane.

Though in principle high-temperature thermal cracking drives the system to methane, not enough hydrogen is available for complete conversion of all of the carbon to methane. Using heptane as a simple model, its conversion to methane could be written as

$$C_7H_{16} \rightarrow 4CH_4 + 3C_5$$

where C represents the anticipated accompanying graphitic carbon solid. If formation of methane accounts for all of the hydrogen, some carbon is necessarily left. Alternatively, consider that all the heptane were consumed in formation of methane:

$$C_7H_{16} + 12H \rightarrow 7CH_4.$$

Thinking of the process in this way leads to the question of where the extra hydrogen comes from.

Hydrogen does not occur in natural systems as  $H_2$ . Hydrogen necessary to drive the conversion of heptane to methane must come from radical processes during catagenesis. Such internal transfer of hydrogen necessarily results in the formation of carbon-rich products. Radical disproportionation and hydrogen abstraction reactions help drive these changes. Disproportionation of a radical formed by C–C bond scission during catagenesis can be represented as

$$2R-CH_2-CH_2-CH_2 \bullet \rightarrow R-CH_2-CH_2-CH_3+R-CH_2-CH=CH_2.$$

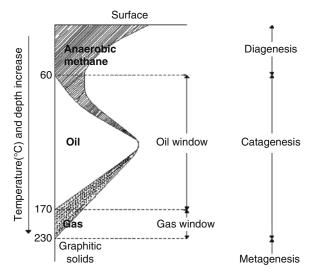
Loss of a hydrogen atom from the alkene product would occur at the allylic position:

$$R-CH_2-CH_2-CH=CH_2+R' \rightarrow R-CH_2-CH \rightarrow CH=CH_2+R'H$$

The allyl radical could disproportionate further to give a diene,  $R-CH=CH=CH=CH_2$ . Further loss of hydrogen could produce trienes and cyclic compounds. Eventually, aromatic hydrocarbons form. Even more hydrogen becomes available as the benzene rings fuse into larger, polycyclic aromatic ring systems, which in turn continue the transformation toward graphite. Benzene has an atomic H/C ratio of 1, naphthalene 0.80, and phenanthrene or anthracene, 0.71. Hydrogen lost from cyclization, aromatization, and growth of aromatic ring systems results in the progression of those molecules toward graphite. Hydrogen lost from these processes is consumed in conversion of kerogen to smaller hydrocarbon molecules and ultimately to methane.

The entire sequence of diagenesis and catagenesis involved in production of oil and gas, is summarized in the kerogen maturation diagram, Figure 8.6. The vertical axis represents increasing depth within the Earth and, because of the natural geothermal gradient, therefore also represents increasing temperature. The first product of interest is biogenic methane, formed in the biochemical reactions of diagenesis. As pyrolytic decomposition of kerogen proceeds, eventually there appear products of molecular size small enough to be liquid at ordinary conditions – the material referred to as petroleum or crude oil. Oil formation in catagenesis begins at a depth corresponding to about 60 °C, and said to be the opening of the oil window.

Oil formed at the opening of the oil window represents only a limited extent of catagenesis. It will contain relatively large molecules, so can be expected to be viscous, of relatively high density, and having a high boiling temperature range. (Relationships between molecular structure and physical properties are discussed further in Chapter 9.) As catagenesis continues, molecular components of the oil become



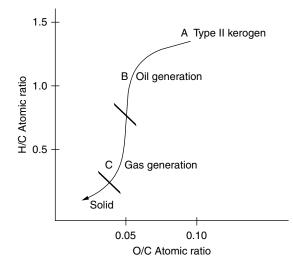
**Figure 8.6** Formation of oil and gas is accounted for by the production of methane by anaerobic bacteria near the surface, the opening of the oil window at  $\approx 60$  °C, beginning of some gas formation at or near the maximum in oil production, closing of the oil window at  $\approx 170$  °C, and closing of the gas window at  $\approx 225$  °C.

progressively smaller and, therefore, lower in boiling range, viscosity, and density. Simultaneously with the formation of lighter oils, and eventually gases, of increasing H/C, highly aromatic compounds of decreasing H/C must also form. This suggests that light oils should contain high concentrations of aromatic compounds, and yet they do not.

The fact that light oils are not highly aromatic results from solubility differences. An old and useful rule of chemistry is that "like dissolves like." As the system evolves to increasingly light, aliphatic molecules and – necessarily at the same time – to increasingly larger, aromatic molecules, the aromatics become less soluble in the H-rich oil. Eventually, as catagenesis continues, aromatics can form a separate phase. In the laboratory, addition of pentane, hexane, or heptane to petroleum can cause separation of a high molecular weight, aromatic phase, called asphaltenes. In nature, presence of large amounts of light hydrocarbons, or gas, can precipitate asphaltenes from the oil, a process called deasphalting. Asphaltenes in turn transform to natural asphalts and other highly aromatic, high density, viscous materials.

At about 170 °C the oil window closes; the only catagenesis product is gas. This transition represents the opening of the gas window. At  $\approx$ 225 °C formation of gas ceases. The final product is a carbonaceous, highly aromatic solid.

Gas formation occurs in two regions of the kerogen maturation diagram: biogenic gas forms during diagenesis, and additional gas results from catagenesis. The only hydrocarbon component of the biogenic gas is methane, because methane comes from specific biochemical reactions for which it is the only gaseous hydrocarbon product. In comparison, as catagenesis proceeds deeper into the oil window, some of the small products of cracking are molecules that are gaseous at or near ambient temperatures, including ethane, propane, butane, and possibly even pentane through heptane. Gas from near the middle to bottom of the oil window is a mixture of these light



**Figure 8.7** The van Krevelen diagram allows tracking of compositional changes in the catagensis of kerogen, as shown here for Type II kerogen. This type of diagram complements Figure 8.6.

hydrocarbons. The more severe the catagenesis, the greater the likelihood that even the gaseous  $C_2$ – $C_7$  molecules will crack to methane. Downward through the gas window, the gas becomes more and more methane-rich. Gas in which methane is the predominant, or even exclusive, hydrocarbon product is found near the bottom of the gas window.

Dominant components of any kerogen are carbon, hydrogen, and oxygen. In principle, compositional changes during catagenesis could be followed by plotting the amounts of these elements on a ternary diagram or on three-variable Cartesian coordinates. However, it is convenient to reduce the three variables to two by using ratios. In this way, changes in composition can be represented in the familiar format of a two-coordinate graph. By convention, the standard approach plots H/C atomic ratio against O/C atomic ratio. Such plots are known as van Krevelen diagrams [F]. The van Krevelen diagram for the catagenesis of Type II kerogen is shown as Figure 8.7.

Graphite (for which H/C = O/C = 0) lies at the origin of a van Krevelen diagram. Initial transformations in early catagenesis, where thermally labile functional groups are lost as  $CO_2$  and  $H_2O$ , appear as region A of Figure 8.7. Oil formation occurs in region B, gas formation, in region C. As these changes take place, the remaining material becomes increasingly carbon-rich, heading, as the curve indicates, toward the origin.

Sediments containing more than 1% of Types I or II kerogen constitute two additional kinds of fuel precursor: the oil shales, with 2-50% kerogen, and the coals, with >50% kerogen. Oil shales are sapropelic, meaning that non-marine algae constitute the principal contributors to the kerogen. The term "sapropelic" derives from a Greek word meaning "rotten," as if this amorphous, partially decomposed material had formed by rotting. Incorporation of sapropelic organic matter into inorganic sediments results in transformation of the mixture to the material called oil shale (Figure 8.8).



Figure 8.8 A specimen of oil shale. Despite what the name may imply, there is no oil *in* oil shale; this is a relatively kerogen-rich material capable of yielding oil upon heating.

Unfortunately, the term "oil shale" is not often accurate, in that few, if any, of these sediments actually contain liquid oil, and the inorganic portion is not shale. The inorganic material contains various minerals, such as quartz, aluminosilicates, or carbonates. Oil shale could contain up to 50% organic matter, though usually the content is lower than this. Oil shales considered for commercial exploitation contain  $\approx 30\%$  organic matter. The organic matter has a composition typically in the range 70–80% carbon, 7–11% hydrogen, 1–2% nitrogen, 1–8% sulfur, and 9–17% oxygen. For a given carbon content, an oil shale has greater hydrogen content and less oxygen than coal.

Oil shales resemble coals more than oil source rocks, because significant oil yield is not achieved until temperatures in the vicinity of 350 °C are reached. Like coal, oil shale does not melt when heated, but rather undergoes irreversible thermal decomposition. Liquid hydrocarbons produced from oil shale resemble petroleum liquids more closely than they resemble liquids from thermal decomposition of coals. Oil from the best quality shales contains a high percentage of alkanes, but often accompanied by high sulfur content. Oxygen and nitrogen contents tend to be higher in oil from shale than in petroleum.

# 8.4 Catagenesis of humic kerogen

Formation of most humic coals derives from conditions prevailing in peat swamps. Organic matter grew and accumulated in bogs, marshes, or swamps in which the water was largely stagnant. Diagenesis converts this accumulated organic matter into peat (Type III kerogen). Peat is found today in enormous deposits in Europe, North America, and parts of northern Asia. It is used for domestic heat, and occasionally in industrial or small utility applications. Peat, as cut from the bog, is more water than organic material (up to 90% moisture in some cases). The calorific value of thoroughly dried peat lies in the range of 20–23 MJ/kg, higher than wood but lower than most coals. The primary consideration favoring use of peat as a fuel is the lack of availability of coal in the region.

Formation and accumulation of peat ends when it is covered by a layer of inorganic sediment. Gradually the layer of sediment thickens, as more sediment accumulates. The

buried peat experiences increasing temperatures from natural geothermal gradients. At the same time, the weight of accumulating, overlying sediments increases the pressure on the peat [G].

With the peat effectively sealed within layers of inorganic sediment, the very long time periods typical of geological processes can operate. Assuming typical geothermal gradients, coals are not likely to experience extreme temperatures. Burial to 10 km would be equivalent to exposure to 100-300 °C. These temperatures seem too low to drive the pyrolysis chemistry; a rule of thumb suggests that pyrolysis reactions become significant at about 350 °C. But, in this instance time is on our side. The long coalforming times allow reactions that would be immeasurably slow on a human time scale to occur in geological time, tens of millions of years for catagenesis of humic kerogen. A reaction with a rate constant of  $10^{-10}$  s<sup>-1</sup> might take three hundred years to get to the first data point in the laboratory, but thirty million years have  $10^{15}$  seconds, a lot of time for even a very slow reaction to occur.

The contribution of substantial amounts of unaltered, or slightly altered, lignin to Type III kerogen provides several important distinctions in catagenesis relative to Types I and II kerogen. First, the atomic H/C ratio of Type III kerogen is distinctly lower than those of Types I and II, typically <1 compared to 1.4–1.8 for Types I and II. From Figure 8.5, this suggests that catagenesis of Type III kerogen will be dominated by carbon-rich products. Second, lignin has a macromolecular structure that survives diagenesis with little transformation. The reactions of catagenesis involve transformations within a macromolecular framework; that is, transformations of solids. Catagenesis of Type III, or humic, kerogen, is often referred to as coalification. The extent of coalification reflects progressively decreasing H/C and O/C ratios, and a steady increase in carbon content. Coalification also results in an increase in coal rank. Though the actual criteria for assigning rank relate to combustion and coking behavior (Chapter 17), for the present discussion, rank can be considered to represent the progression along the path from kerogen to graphite.

Early in catagenesis, materials that survived diagenesis and that participated in formation of humic acids and kerogen begin to break up. Waxes or unreacted fats could hydrolyze if groundwater is present:

# $RCH_2COOCH_2CH_2R' + H_2O \rightarrow RCH_2COOH + HOCH_2CH_2R'.$

The reaction products participate in thermally driven reactions of decarboxylation and dehydration.

Alcohols dehydrate at elevated temperatures in a reaction catalyzed by clay minerals. Clays are abundant in nature, and may have a role in facilitating some of the reactions of catagenesis. Alcohol dehydration can be represented by the reaction

#### $RCH_2CH_2OH \rightarrow RCH=CH_2 + H_2O.$

In the laboratory, this reaction proceeds at about 160 °C. Kerogen buried to 1 km may be exposed to a temperature of about 60 °C, depending on the local geothermal gradient. Applying the rule of thumb that reaction rates double for every 10° rise in temperature, or are halved for a 10° drop, the rate of alcohol dehydration would be reduced by  $(\frac{1}{2})^{10}$ , i.e.  $\frac{1}{1024}$ . A dehydration reaction that could be run in a three-hour laboratory period at 160 °C would take eighteen weeks in nature at 60 °C, still extremely fast on a geological time scale.

Acids decarboxylate at high temperatures:

$$RCH_2COOH \rightarrow RCH_3 + CO_2$$
.

Thermal decarboxylation of acids is performed in the laboratory at 300–400 °C. Kerogens usually do not experience such high temperatures during catagenesis, but, again, the much lower reaction rates anticipated for temperatures typical of catagenesis (i.e.  $\approx$ 100–200 °C) still offer substantial conversion over periods of thousands to millions of years.

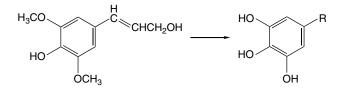
Esters also experience thermally induced decarboxylation, the immediate products being an alkene and an acid, e.g.

$$R'CH_2CH_2OOCR \rightarrow R'CH=CH_2 + HOOCR.$$

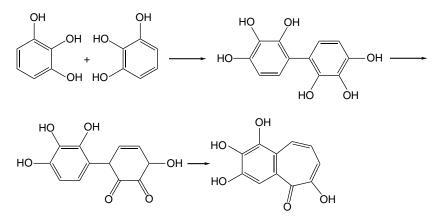
Since the acid formed in this reaction will probably decarboxylate, the final products will be an alkane, an alkene, and carbon dioxide. Using one of the components of carnauba wax as an example:

$$CH_3(CH_2)_{22}COOCH_2CH_2(CH_2)_{29}CH_3 \rightarrow$$
  
$$CH_3(CH_2)_{21}CH_3 + CH_2 = CH(CH_2)_{29}CH_3 + CO_2.$$

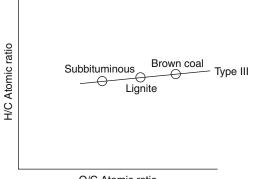
Partial degradation of lignin could result first in liberation of the monomeric constituents, followed by further degradation reactions. Using sinapyl alcohol as an example:



A possible reaction product, 1,2,3-trihydroxybenzene (pyrogallol), could undergo self-condensation, e.g.

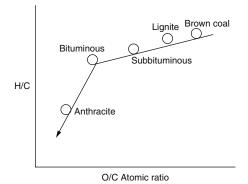


The overall process results in condensation of cyclic compounds into larger, multiring systems, accompanied by the loss of carbon dioxide.



O/C Atomic ratio

**Figure 8.9** The early stages of coalification (catagenesis of Type III kerogen) result in formation of brown coal, lignite, and subbituminous coal along a line of gentle slope on the van Krevelen diagram.



**Figure 8.10** As coalification progresses, the pathway becomes more steeply sloped with the formation of bituminous coals and then anthracite.

The processes discussed to this point share the common feature of loss of oxygen in small, volatile molecules. On a van Krevelen diagram, the effect would be observed as a reaction pathway from the initial kerogen toward the abscissa (i.e. a pathway of decreasing O/C) with a small slope, shown in Figure 8.9. The system is becoming increasingly more carbon-rich, as indicated by the pathway from right to left on the van Krevelen diagram, Figure 8.9.

The hydrogen redistribution process (Figure 8.4) shows that one of the eventual reaction products is graphite, which lies at the origin in a van Krevelen diagram. Consequently, there must be some place along the reaction pathway for Type III kerogen in which a significant change of slope occurs, such that the curve "bends over" and heads toward the origin, shown in Figure 8.10.

Once again, the behavior of simple organic compounds provides insight into what might be expected as catagenesis proceeds. As H/C drops, solid materials form that are less and less soluble, and increasingly refractory (Table 8.5).

Atomic H/C	Example	Physical state at ambient conditions	Melting point, °C	Solubility
1.00	Benzene	Liquid	6	Soluble in or miscible with
0.80	Naphthalene	Solid	80	many common solvents
0.71	Phenanthrene	Solid	100	
0.63	Pyrene	Solid	150	Soluble in few common solvents
0.60	Benzo[e] pyrene	Solid	311	Soluble in chloroform
0.50	Coronene	Solid	434	Dissolves with difficulty in benzene
0	Graphite	Solid	$\approx 3800$	Totally insoluble

**Table 8.5** As atomic H/C decreases among a series of aromatic compounds, they become increasingly refractory and less soluble.

Table 8.6 Comparison of elemental compositions of cellulose, Norwegian spruce lignin, and Brazilian peat.

Sample	Carbon, %	Hydrogen, %	Oxygen, %	Atomic H/C	Atomic O/C
Cellulose	42.1	6.4	51.5	1.83	0.92
Lignin	62.5	5.7	31.7	1.10	0.38
Peat	58.4	6.6	34.6	1.35	0.44

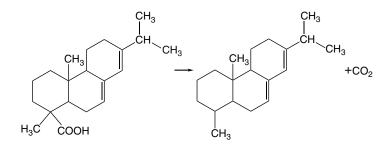
In the maturation of Type III kerogen, these refractory, insoluble materials are the coals.

Type III kerogen (peat) contains, on a mass basis, about 55% carbon, 6% hydrogen, and 35% oxygen, not much different from the compositions of lignin and cellulose, as shown in Table 8.6.

Early catagenesis results in a loss of oxygen and an apparent increase of carbon. (The apparent increase in carbon is an artifact of the inexorable requirement that percentages sum to 100. If the percentage of one component drops, another must rise. No carbon is actually added to the system.) Compression of peat, to about half its initial volume, and reduction of the oxygen content via catagenesis results first in a material usually called brown coal, having an approximate composition of 65% C, 6% H, and 25% O. (Throughout this section the elemental composition is that of the carbonaceous portion of the sediment only. It does not take into account possible incorporation of water or various kinds of mineral with the coal. How this is accounted for, and why, are discussed later, in Chapter 17.) This process takes about thirty million years. Brown coals are important energy resources in central and eastern Europe, and in Australia.

Further compaction, to about one-fourth the volume of the original peat, and further reduction in oxygen leads to lignite [H], approximately 72% C, 6% H, and 20% O. By this point approximately sixty to seventy million years have elapsed. Commercially important deposits of lignite occur in many parts of the world, including Russia and eastern Europe, the United States and Canada, China, Indonesia, India, and Brazil. The dominant application is in boilers for producing steam in electricity generating plants.

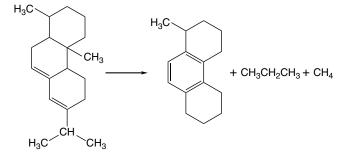
Continued catagenesis beyond lignite includes further loss of carboxyl and methoxyl groups. Components of resins can decarboxylate:



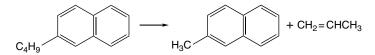
Subbituminous coal, with an elemental composition of about 75% C, 5% H, and 15% O, becomes the next product. One of the world's largest, and commercially most important, deposits of subbituminous coal is the Powder River Basin region of the western United States, which accounts for roughly a third of total U.S. coal production.

Catagenesis beyond the subbituminous stage appears to proceed in a discontinuous sequence of major changes, called coalification jumps. At about  $60 \,^{\circ}$ C, a new set of reactions becomes important. This temperature is about the same as the opening of the oil window in the catagenesis of Types I and II kerogen. The first coalification jump occurs at a composition of about 80% carbon. This point represents the beginning of the composition range of the bituminous coals, also the point where the significant slope change occurs on the van Krevelen diagram. Hydrogen redistribution begins in earnest, and the H/C ratio begins to decrease.

At the first coalification jump, several types of reaction now become important. Typically, they occur at depths of 1–2 km, or temperatures in excess of 60°C. Continued compression by the layers of overlying sediments reduces an original 7–20 m of peat to about 1 m of bituminous coal. Resins experience partial dealkylation and aromatization:



Side-chain cleavage occurs in alkylaromatics:



Long alkyl chains of lipids, or lipid-derived materials, undergo thermal cracking, e.g.:

$$C_{27}H_{56} \rightarrow C_{13}H_{26} + C_{14}H_{30}.$$

Each of these examples incorporates the expected hydrogen redistribution. Cracking of *n*-butylnaphthalene (H/C 1.14) produces methylnaphthalene (H/C 0.91) and propylene (H/C 2.00). And, cracking of heptacosane (H/C 2.07) yields, in this example, tridecene (H/C 2.00) and tetradecane (H/C 2.14).

These reactions result in the formation of some light products, which can escape from the system, but also result in a reduction of H/C ratio in the material remaining. With reduction of H/C becoming now more important than decreasing O/C, this effect creates the slope change on the van Krevelen diagram.

The first coalification jump marks the beginning of the formation of the most important coals in commercial use, the bituminous coals. Bituminous coals are the most abundant, and have the greatest commercial importance, of the world's coals. As with all coals, their dominant use nowadays in industrialized nations is for raising steam in electricity generating plants. Conversion to coke for use as a fuel and reducing agent in the metallurgical industry – especially iron and steel – is the second most important use of bituminous coals.

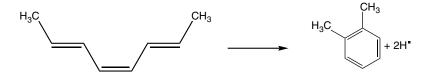
Carbon dioxide was the principal gaseous product of the formation of brown coal, lignite, and subbituminous coal. Beyond the first coalification jump, methane becomes the principal gaseous product. Measuring the  $CH_4/CO_2$  ratio of gases trapped in a coal deposit provides a good indication of its geological maturity. With this shift in the nature of gaseous products, the principal change in composition of the solid now becomes loss of hydrogen, with relatively less oxygen loss. On a van Krevelen diagram this appears as a significant drop in H/C with less pronounced drop in O/C, the effect responsible for the continuing marked slope change as the reaction path moves toward the left.

The second coalification jump occurs at carbon contents of approximately 87%. Loss of oxygen occurs, probably by destruction of phenolic functional groups. Significant production of methane also occurs. The temperature at this depth is likely to exceed 120 °C. As methane, with its H/C of 4.00, forms, the H/C ratios of the remaining products of reaction become progressively lower. Consider a hypothetical sequence of reactions that produce methane, beginning with undecane:

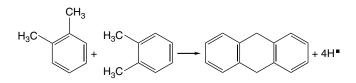
$$\begin{split} & C_{11}H_{24} \to CH_4 + C_{10}H_{20}, \\ & C_{10}H_{20} \to CH_4 + C_9H_{16}, \\ & C_9H_{16} \to CH_4 + C_8H_{12}. \end{split}$$

The products, going sequentially from decene to nonadiene to octatriene, have progressively lower H/C ratios, 2.00, 1.77, and 1.50, respectively. In principle, only three more molecules of methane could be formed, until the remaining product has H/C of 0.

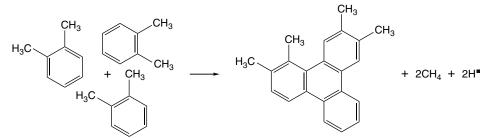
The carbon-rich reaction products become increasingly unsaturated, undergoing cyclization and aromatization. An example could be conversion of 2,4,6-octatriene to *o*-xylene:



Aromatization also provides a source of hydrogen to meet the requirements for the H-rich products. Still more hydrogen can be obtained by growth of polycyclic aromatic systems, such as conversion of *o*-xylene to 1,2-dimethyl-9,10-dihydroanthracene,

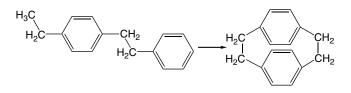


or to 1,2,4,5-tetramethyltriphenylene:

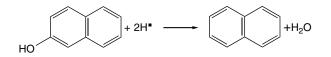


where, in this step, H/C is reduced further, from 1.25 to 0.90.

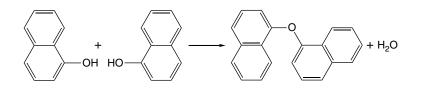
Vertical alignment of aromatic rings begins, for which the family of stacked aromatic ring compounds, the cyclophanes, serves as a possible example



Loss of oxygen continues, as by the deoxygenation of phenols:

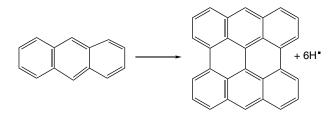


possibly also accompanied by ring condensation:

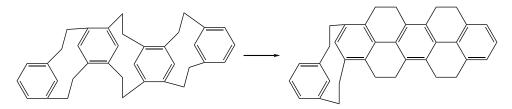


The third coalification jump, at a carbon content of about 91%, marks the beginning of anthracite formation. High temperatures and, possibly, high pressures are involved.

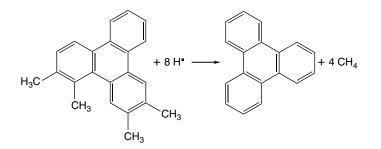
Virtually all commercial deposits of anthracite in the world are found in mountainous regions where extensive folding of the rocks has occurred. The high pressures generated by the rock folding may have contributed to anthracite formation. Extensive formation of methane occurs, up to  $\approx 200$  l per kilogram of coal. Methane may come from stripping the remaining methyl groups away from aromatic ring systems. Further aromatization of ring systems, and further condensation of aromatic rings into polycyclic aromatic systems, occurs. Vertical alignment or stacking of aromatic ring systems accompanies these processes. Condensation of aromatic rings is exemplified by the dehydrogenative polymerization reaction of anthracene:



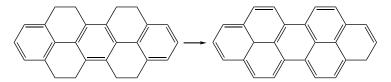
In addition, compounds having vertical stacking of aromatic rings continue to react to produce larger ring systems. In cyclophane chemistry, compounds containing four stacked aromatic rings can convert to products having much larger ring systems, e.g.:



The severe reaction conditions can drive the demethylation of aromatic rings:

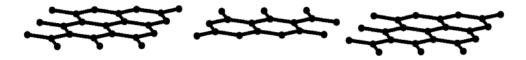


Demethylation is accompanied by continued condensation of ring systems as illustrated for the dehydrogenative polymerization of anthracene, and continued vertical alignment of ring systems. The process may have taken several hundred million years, and reduces the atomic H/C to about 0.5. Extremes of temperature and pressure form highly aromatic, nearly graphitic solids, e.g.



These anthracites may be three to four hundred million years old, and contain  $\approx 93\%$  carbon.

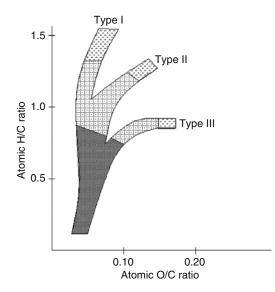
At  $\approx 96\%$  carbon content, formation of meta-anthracite occurs. Aromatization of cyclic structures and their condensation to a nearly graphitic structure has taken place. With enough time and severity of reaction conditions, natural graphites form. Natural graphite is the "ultimate coal." It is pure carbon, with all atoms incorporated into aromatic ring systems and perfectly aligned in a layer structure:



Progression from brown coals through anthracites marks a regular transition along the van Krevelen diagram, particularly characterized by the increase of carbon content, from <70% in brown coals to >90% in anthracites. This makes it possible to classify, or to rank, coals on the basis of the extent to which they have experienced coalification, indicated by their position on the van Krevelen diagram or by their carbon content. Systems of coal rank indeed exist, with brown coal assigned the lowest rank and the anthracite the highest. These rank classification systems are discussed in Chapter 17.

The Earth's geothermal gradient supplies the heat needed for coalification. The deeper a coal is buried, the higher the temperatures it experiences, and the longer it is exposed to these temperatures. Such coal has probably been converted to a high rank. Since burial requires long geological times, usually the deeper a coal has been buried, the older it is. Hilt's rule [I] states that the deeper a coal has been buried, the older it is, and the higher the rank it has attained. Knowing only the age, or the depth, or the rank of a coal makes it possible to infer, at least qualitatively, something about the other two properties. Hilt's rule applies only to a single group of coal seams in a single region that displays no evidence of unusual geological activity. The rule breaks down when comparing coals from different geographical regions, or from areas of unusual geological activity.

Methane forming along with the bituminous coals and anthracite has been a source of serious problems. Slow seepage of methane from the coal into mine air can result in the concentration of methane eventually reaching the explosive limit, about 5–13% methane in air. An inadvertent spark or open flame can set off a methane explosion, which blows coal dust into the air and immediately causes a devastating, secondary dust explosion [J]. Miners use the name *firedamp* to refer to the methane seeping from coal. Many thousands of miners around the world have lost their lives to methane explosions, and still do to this day, despite the hazards of firedamp being recognized for centuries [K]. Accumulated methane held at high pressure in coal seams can sometimes be released with near-explosive force when continual removal of the coal eventually reduces the mechanical strength of the remaining coal to a point at which the high pressure can no longer be contained. Then, the accumulated methane bursts loose, blasting ahead of it any coal or rock remaining in the way. Miners call this phenomenon



**Figure 8.11** A summary van Krevelen diagram showing the transformations of the three main types of kerogen into gases, oils, and carbonaceous solids. Gas or oil that has migrated away from the kerogen is not accounted for in this diagram.

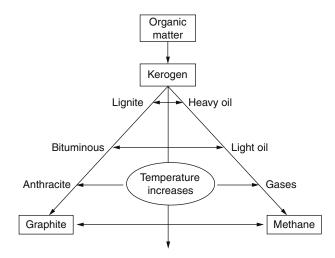
an *outburst*. An outburst will generate high-velocity, flying fragments of coal or rock, potentially lethal to anyone haplessly working nearby. A third problem is that methane is a greenhouse gas; though not so notorious as carbon dioxide, it is even more potent at absorbing infrared radiation. The slow emission of methane from coal seams, or its deliberate removal by circulating large volumes of air through a mine to keep methane below the explosive limit, can contribute to the greenhouse effect.

On the other hand, methane is a superb fuel. If only for this reason, it can be useful to drain the methane from coal seams for use as a fuel. The term *coalbed methane* is used to refer to methane trapped in coal and recovered as a fuel source. Of course, recovering coalbed methane also improves safety in the mine and reduces methane emissions to the atmosphere.

#### 8.5 Summary

The transformations of kerogens can be summarized on a single van Krevelen diagram, see Figure 8.11.

All kerogens show an initial region of  $CO_2$  and  $H_2O$  formation via decarboxylation and dehydration. Types I and II kerogen show a long region of oil formation. Oil migrates out of the source rock, and is lost from further catagenetic reactions. (Oil can experience further reactions during or after its migration, but those are not part of the catagenesis of the kerogen.) The reaction pathways shown in Figure 8.11 represent the changes in composition of the remaining organic material. Oil or gas that has migrated away does not appear in this diagram. Some oil could be formed from Type III kerogen, though not usually thought of as being oil source rocks. Any kerogen can form gas. Extensive gas formation accompanies severe thermal decomposition of the



**Figure 8.12** As severity of catagenesis increases, as measured by temperature for example, the main products from Types I and II kerogen often correlate with those from Type III, e.g. heavy oils with lignites, or gas with anthracites.

organic material. As gas production continues, the solid becomes increasingly graphitelike. The occurrence of oil and gas together is not uncommon, and is a feature of the lower half of the oil window.

Provided that the appropriate organic source materials were available in the same geographic region, coal, oil, and gas could occur together. As the combined effects of temperature and time increase, coal rank also increases. As temperature increases, cracking of oil to progressively lighter oils increases, eventually forming gas. Thus as the rank of coal increases, any oil that might be associated with it becomes lighter. At the high end of the rank range, associated with high reaction temperatures, long reaction times, or both, it would be reasonable to expect coal and gas to be associated, but no oil. This relationship is shown in Figure 8.12.

Examples of this occur in the world. The Williston Basin, which encompasses a broad area of western North Dakota, eastern Montana, and southern Saskatchewan, has heavy oil and lignite. The gas in the Slochteren field of the Netherlands probably came from catagenesis of deeply buried coals that underlie the gas deposits. The Mahakam Delta region of Indonesia, mentioned previously, is also a rich source of oil and gas.

#### Notes

[A] From time to time proposals have been made that fossil fuels have non-biological sources. These ideas have been advanced by a range of individuals, from brilliant scientists such as Dmitri Mendeleev and Marcelin Berthelot to outright loonies. Mendeleev postulated that reactions of carbon at very high temperatures of Earth's mantle could produce metal carbides, such as CaC<sub>2</sub>. In the crust, carbides could react with water to form acetylene, e.g. CaC<sub>2</sub> + 2 H<sub>2</sub>O  $\rightarrow$  Ca(OH)<sub>2</sub> + C<sub>2</sub>H<sub>2</sub>. Acetylene can trimerize to benzene, or react in other ways to form long-chain

hydrocarbons. All of these reactions can be performed in the laboratory, but are not believed to have a significant role in petroleum formation. At the other end of the spectrum, it has been suggested that, billions of years ago, as Earth was forming by the accretion of material in space, this proto-planet somehow passed through a cosmic rainstorm of petroleum in outer space, acquiring in the process vast pools of oil.

- [B] Nowadays coal is found in Antarctica and the far-northern island of Spitsbergen, and oil is abundant in the arid Middle East. These facts show that both Earth's climate and the relative positions of landmasses can vary significantly over geological time.
- [C] The same chemical process can occur in organic matter accumulated in landfills. It gives rise to two problems. Methane is flammable, and, in certain proportions, methane-air mixtures are explosive. Methane generation in significant quantities becomes a safety hazard. Second, methane is a potent greenhouse gas. Methane from landfills can contribute to global climate change. However, enterprising fuel engineers have found ways of extracting and capturing the methane from landfills, and using it as a fuel source. Gas used in this way has the trivial name *landfill gas*. Deliberately extracting landfill gas provides another source of fuel, and at the same time reduces safety hazards and greenhouse gas emissions. Aside from landfills, other sources of organic matter, such as agricultural wastes, can be subjected deliberately to anaerobic digestion and lead to the production of useful fuel gas.
- [D] Seeing intermittent flashes of light in a swamp or marsh has been the origin of numerous lurid stories of ghosts, goblins, or other supernatural effects. One such relates to the aptly named Great Dismal Swamp on the border of Virginia and North Carolina in the United States. There, the light flashes were attributed to a brakeman on the former Norfolk and Western Railway, who had somehow fallen onto the track, such that a passing train cut his head off. The light was said to be the ghost of the now-headless man, swinging his lantern, searching for his severed head.
- [E] In 1867 phenol, known by its trivial name carbolic acid, was the first germicide and disinfectant introduced to surgery, by the great British doctor Sir Joseph Lister (1827–1912). Remarkably, ingestion or absorption of phenol through the skin can cause serious health effects and even be fatal in relatively small amounts (≈15 g). 2-Methoxy-4-methylphenol (creosol), one of the phenols present in creosote, is a widely used antiseptic and disinfectant.
- [F] Dirk van Krevelen (1914–2001), a Dutch scientist, enjoyed a remarkable and remarkably diverse career in several fields, and held various management positions, including being director of research for the Dutch state mines, and later head of research and development for the company that is now Akzo. Even while actively engaged in management, he contributed numerous papers to the scientific literature, and produced two landmark books, one on coal and one on polymers.
- [G] There does not seem to be a strong consensus on the role of pressure in coal formation. Some coal geologists have suggested that extreme tectonic pressures associated with mountain formation might accelerate coalification. Others have argued that pressure might retard some of the chemical reactions in coalification, though possibly affecting the physical properties of the coal.
- [H] In some coal literature, particularly from outside the United States, the terms lignite and brown coal are used synonymously. However, others argue for a distinction

between the two, based on, e.g. the slightly lower carbon content of brown coal, and its much higher associated moisture in an as-mined condition.

- [I] Named for the German geologist Carl Hilt, who published this law in 1873. Virtually no information is available on his life and career in the modern literature, save for a street named for him in Herzogenrath, in northwestern Germany near Aachen.
- [J] The person who first recognized the seriousness of firedamp in coal mines is lost to history, but the person to first take measures against it was Sir Humphry Davy (1778–1829). Stimulated by a horrific explosion in the Felling mine near Newcastle upon Tyne, Davy developed, around 1815, a safety lamp that used metallic gauze to prevent heat of the lamp's flame from igniting a methane-air mixture. The Davy lamp, or variations of it, was standard miners' equipment until it was replaced by electric lamps. Davy made a great many other contributions to science, including clearly recognizing the importance of air for the decay of organic matter (though in Davy's era the role of aerobic microorganisms was not known). Davy's greatest contribution to science by far was his giving Michael Faraday an opportunity as a laboratory assistant; Faraday became certainly one of the greatest of the nineteenth century chemists and physicists.
- [K] Many underground coal mines once employed a person known as the fire boss. His job was to enter the mine, alone, about two hours before the start of a working shift and test for the presence of firedamp by checking for a characteristic change in color of the flame in his lamp. The fire boss could either certify that a particular passage in a mine was safe for work that day, or could bar miners from entering if the firedamp concentration was too high. This job must have required remarkable levels of fortitude.

#### References

- [1] Smil, Vaclav. Energy in Nature and Society. MIT Press: Cambridge, 2008; Chapter 3.
- [2] Combaz, A. Les kérogènes vus au microscope. In: *Kerogen*. (Durand, Bernard, ed.) Éditions Technip: Paris, 1980; Chapter 3.

#### **Recommended reading**

- Berkowitz, Norbert. *Fossil Hydrocarbons*. Academic Press: San Diego, 1997. Chapter 2 of this book focuses on origins of fossil fuels, including the oil sands, asphalts, and sapropelic coals.
- Bouška, Vladimír. *Geochemistry of Coal*. Elsevier: Amsterdam, 1981. Roughly the first half of this book is devoted to coalification processes.
- Dukes, J.S. Burning buried sunshine. *Climatic Change*, 2003, **61**, 31–44. A very useful discussion concerning the enormous amounts of organic matter that had to have accumulated to produce the fossil fuels we utilize today.
- Durand, Bernard. (ed.) *Kerogen*. Editions Technip: Paris, 1980. A collection of chapters from various authors, relating to various aspects of kerogen formation, composition, and characterization.
- Engel, Michael H. and Macko, Stephen A. (eds.) *Organic Geochemistry: Principles and Applications*. Plenum Press: New York, 1993. This book is an edited collection of chapters by different authors, many of the chapters dealing in great detail with diagenesis and thermal alteration of organic matter.

- Given, Peter H. An essay on the organic geochemistry of coal. In: *Coal Science. Volume 3*. (Gorbaty, Martin L., Larsen, John W., and Wender, Irving, eds.) Academic Press: Orlando, 1984; pp. 65–252. A tour-de-force of ideas on coal formation and structure, supplemented with extensive references.
- Levorsen, A.I. *Geology of Petroleum*. W.H. Freeman: San Francisco, 1954. An old book, but a classic in its field. Chapter 11 discusses the origin of petroleum.
- Mackenzie, Fred T. (ed.) *Sediments, Diagenesis, and Sedimentary Rocks*. Elsevier: Amsterdam, 2005. This book is also a collection of chapters by various authors. Chapters 8 and 9, on coal formation and on oil and gas, respectively, are thorough discussions relevant to the present chapter.
- Murchison, Duncan G. and Westoll, T. Stanley. *Coal and Coal-bearing Strata*. Oliver and Boyd: Edinburgh, 1968. Though now dated in part, this book still provides a good, solid review of coal geology.
- Nardi, James B. *Life in the Soil*. University of Chicago Press: Chicago, 2007. To look at what happens to the "other" 98% of organic matter that actually does decay, this book provides much useful and interesting information on the roles of various organisms in breaking down accumulated organic matter.
- North, F.K. Petroleum Geology. Allen and Unwin: Boston, 1985. Chapters 6 and 7 in this useful text discuss organic matter and its accumulation, and then conversion to petroleum.
- Selley, Richard C. *Elements of Petroleum Geology*. W.H. Freeman: New York, 1985. An excellent introductory text in the field. Chapter 5 discusses the origin of petroleum.
- Speight, James G. *The Chemistry and Technology of Petroleum*. Marcel Dekker: New York, 1991. A very useful book on most aspects of petroleum. Chapter 2 is of particular relevance here.
- Thomas, Larry. *Handbook of Practical Coal Geology*. Wiley: Chichester, UK, 1992. Chapter 3 is particularly useful; several other chapters also expand on the discussion presented here.
- van Krevelen, D.W. *Coal: Typology–Physics–Chemistry–Constitution*. Elsevier: Amsterdam, 1993. The best book on coal. Chapters 3 through 7 are pertinent to the material discussed here.

# 9 Structure–property relationships among hydrocarbons

#### 9.1 Intermolecular interactions

Virtually all substances of interest in fuel chemistry consist of covalently bonded molecules. Many are hydrocarbons in the literal sense of the word – compounds containing only hydrogen and carbon atoms. Others contain one or more heteroatoms, i.e. atoms of oxygen, nitrogen, or sulfur. Physical properties of fuels have numerous important roles in fuel technology and utilization, e.g. boiling point, because distillation is commonly used for separations; density, because the amount of fuel that can be carried on vehicles or aircraft is limited by volume and not by mass; and viscosity, because we need fluids to flow, or to be pumped, from place to place. An understanding of how chemical composition and molecular structure influence physical properties shows that the properties of substances do not come about by some haphazard chance but rather because of fundamental links between composition, structure, and properties. Further, such links provide useful guidelines or rules of thumb for estimating expected properties from composition, or vice versa.

The most noticeable property of most substances is their physical state: solid, liquid, or gaseous. The first point of inquiry becomes that of why molecules form solids or liquids at all. Why isn't everything a gas? To exist in a condensed phase, i.e. as a liquid or solid, there must be attractive forces among molecules strong enough to hold them in proximity.

In some molecules, the center of positive charge and center of negative charge do not coincide. Water serves as an excellent example. Such molecules possess a permanent electric dipole moment. This effect arises because atoms have different electronegativities. On the Pauling electronegativity scale [1], for example, oxygen has a value of 3.5 and hydrogen, 2.1. Because the oxygen atom has the greater ability to attract electrons, in the water molecule the center of negative charge is close to the oxygen atom, and the center of positive charge is closer to the hydrogen atoms, giving rise to a dipole moment. Polar molecules can attract each other via the electrostatic interactions of the dipoles.

Table 9.1 gives the Pauling electronegativities of elements of chief interest in fuel chemistry.

There is a slight difference in electronegativity between carbon and hydrogen, but carbon-hydrogen bonds have only a small dipole. Consequently, alkanes have no permanent dipole moment [A]. However, there must be some kind of interaction between such molecules, because otherwise they would not exist in condensed phases. The weak, short-range interactions between molecules, arising from electrostatic interactions, are generally known as van der Waals forces [B], see Figure 9.1.

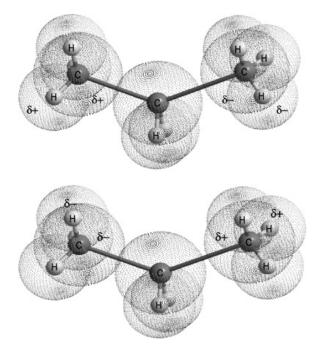
Element	Electronegativit	
Carbon	2.5	
Hydrogen	2.1	
Oxygen	3.5	
Nitrogen	3.0	
Sulfur	2.5	

 
 Table 9.1 Values of electronegativity of elements of main interest in fuel chemistry, based on Pauling's scale.

Molecules with permanent dipole moments can induce dipoles in non-polar molecules, establishing an electronic interaction between the permanent dipole in one molecule and the induced dipole in the other. The strength of this interaction depends on how easily a dipole can be induced in the non-polar molecule, i.e. on its polarizability. Polarization involves deformation of the electron cloud in the molecule. Polar molecules induce dipoles on neighboring, non-polar molecules because the electric field of the permanent dipole polarizes the non-polar molecule, causing a small dipole to be induced in the latter.

In molecules with no permanent dipole moment, the motion of electrons in atoms establishes temporary dipoles that continuously change and have very short lifetimes. The temporary dipoles can induce equally short-lived and continuously changing dipoles in neighboring polarizable molecules. This situation also gives rise to electrostatic interactions, albeit very weak ones, between molecules. Though, on average, distribution of charge in a non-polar molecule is uniform, electrons are constantly in motion. At one instant of time, the electron distribution may, temporarily, be slightly non-uniform, such that one portion of the molecule has a slight negative charge, and another portion a slight positive charge. In that instant of time the molecule has a small dipole moment. This small and fleeting dipole can induce a corresponding dipole in a neighboring, polarizable molecule. This effect occurs because the temporary charge accumulated in the molecule distorts the electron distribution in the neighboring molecule. Both the magnitude and orientation of the temporary dipole change constantly, yet the dipole in the neighboring molecule will follow suit and change as well. As a result, the electrostatic interaction between the two molecules does not go to zero. Interactions of the induced dipole in one molecule with that in a neighboring molecule are called dispersion forces, or London forces [C]. Though the induced dipoles constantly fluctuate, they produce attractive interactions between non-polar molecules. London forces are very weak, but nonetheless have a key role in determining and affecting many of the physical properties of compounds of interest in fuel chemistry. In contrast to ordinary electrostatic interactions, which depend on the square of the distance between charges, London forces depend on the sixth power of the intermolecular distance.

London forces represent the weakest intermolecular interactions. The strongest are hydrogen bonds. In molecules having a hydrogen atom bonded to a small, highly electronegative atom (usually an atom of nitrogen, oxygen, or fluorine), very strong interactions can occur between the hydrogen atom and a non-bonding pair of electrons on an electronegative atom in a neighboring molecule. In water, a hydrogen bond



**Figure 9.1** The origin of van der Waals forces between two molecules of propane. The transitory partial dipoles in one molecule induce dipoles in a neighboring molecule.

is established when a hydrogen atom covalently bonded to one water molecule interacts with an electron pair on the oxygen atom of a neighboring molecule. Hydrogen bonds are about an order of magnitude weaker than covalent bonds; they have strengths of about 4–40 kJ/mol, compared to 300–400 kJ/mol for many covalent bonds, but are much stronger than interactions between molecules having permanent dipole moments or London-force interactions. Though fluorine has no significant role in fuel chemistry, oxygen and nitrogen certainly do. Hydrogen bonding has ramifications in several aspects of the physical and chemical behavior.

## 9.2 Volatility

The volatility of normal alkanes serves as a useful base case for comparing the behavior of the other classes of compounds of interest – branched-chain alkanes, cycloalkanes, aromatics, and heteroatomic compounds. *n*-Alkanes have no dipole moment, but do have a polarizable electron cloud, which allows the existence of London-force interactions among molecules. A plot of the normal boiling point [D] of *n*-alkanes as a function of number of carbon atoms in the molecule (Figure 9.2) provides a convenient way of expressing the volatility relationships in this family of compounds.

Several factors account for the relationship shown in Figure 9.2. First, the boiling point of any compound gives at least an approximate indication of the strength of intermolecular interactions, because the boiling point is the temperature at which thermally induced motions of the molecules become large enough to overcome those

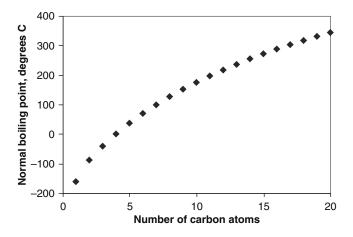


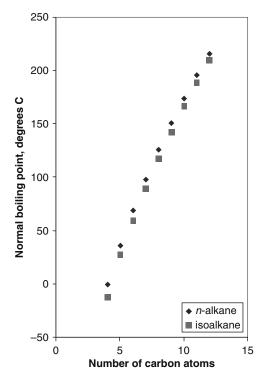
Figure 9.2 The normal boiling points of the first twenty *n*-alkanes as a function of the number of carbon atoms in the molecule.

attractive forces, overwhelming the forces responsible for the existence of the condensed phase. The very short range London forces begin to come into play when the surface of one molecule approaches the surface of neighboring molecules. A large molecule necessarily has a greater surface area, and hence a greater surface of its polarizable electron cloud. The larger the alkane molecule, the more London-force interactions it can experience with neighboring molecules. Since the London-force interactions are stronger between large molecules, large molecules have higher boiling points than their smaller homologs.

A second factor involves mass: molecules of greater molecular mass require more thermal energy to acquire velocities large enough to allow them to escape from the liquid phase. The number of carbon atoms in a molecule relates directly to its molecular mass. Thus molecular mass also makes a contribution to the value of the boiling point. The increase in boiling point as the size of the alkane increases results from the two factors of increasing London forces and increasing molecular masses.

The remaining point is why the trend shown in Figure 9.2 displays a steady, though gradual, decrease in slope. Methane is a small molecule, experiencing only very weak London-force interactions, so not surprisingly has a very low boiling point,  $-162 \,^{\circ}$ C. Ethane, compared to methane, is a molecule just about twice as large. The molecular mass of ethane nearly doubles relative to that of methane, 30 vs. 16 Da. More thermal energy is required to give ethane enough kinetic energy to escape the liquid state. Ethane also has a greater number of electrons that could participate in induced dipoles. And, since ethane is physically a larger molecule, there is more surface over which these induced dipoles can operate. For these reasons, ethane boils at a point well above methane,  $-88 \,^{\circ}$ C.

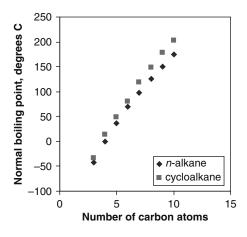
Comparing propane to ethane extends these arguments: increased molecular mass; the greater number of electrons providing greater opportunity for induced dipoles; and greater surface area giving greater attraction among induced dipoles. Hence propane boils at a higher temperature than ethane, -42 °C. Similar arguments would apply to butane (boiling point -0.5 °C) in comparison with propane. But already another effect is at work. Ethane has a molecular mass nearly double that of methane.



**Figure 9.3** Comparison of the boiling points of the 2-methyl branched alkanes (isoalkanes) with the *n*-alkane analogs, as a function of number of carbon atoms in the molecule. Smaller molecules show a distinctly lower boiling point for the branched isomer, the difference diminishing as molecular size increases.

The increase in mass from ethane to propane is only 47%, and, from propane to butane, 32%. Moving along the homologous series of *n*-alkanes can be thought of as extending the size of the molecule by one methylene group,  $-CH_2$ -. From one alkane to the next, the proportional effect of the additional methylene group on molecular size and mass steadily diminishes. With pentane, molecular size is large enough for this compound to be liquid at ordinary ambient conditions, boiling at 36°C. As molecules continue to increase in size, the effects of the three factors – molecular mass, greater opportunities for induced dipoles, and greater surface area – eventually reach a point at which the compound is solid at ambient conditions. Heptadecane, for example, melts at 22°C.

The effects of chain branching reflect differences in molecular surface area, which in turn relate to the strength of London-force interactions. The number of possible alkane isomers increases greatly with increasing number of carbon atoms: there are three isomeric pentanes, 75 isomers of decane, and 366319 isomers of eicosane. The iso- compounds, i.e. alkanes with a single methyl branch at the 2- carbon, make a good starting point. The simplest possible iso- compound is 2-methylpropane, widely known by its trivial name, isobutane. Figure 9.3 compares the normal boiling points of the iso-compounds up to 2-methylundecane with their *n*-alkane analogs.



**Figure 9.4** Comparison of the normal boiling points of *n*-alkanes with cycloalkanes of the same number of carbon atoms. Cycloalkanes show consistently higher boiling points.

Figure 9.3 illustrates two points. First, the boiling points of the iso- compounds are invariably lower than the corresponding *n*-alkane. Since the molecular weights have to be identical, the explanation lies in reduced London-force interactions, the reduction coming from a smaller surface area of the iso- compound. Second, with increasing molecular size, the difference in boiling points between an *n*-alkane and the corresponding iso- compound diminishes, e.g. a difference of  $12^{\circ}$  between *n*- and isobutane to  $6^{\circ}$  from *n*-dodecane to 2-methylundecane. This effect results from the structure of the iso- compound becoming more like the *n*-alkane as further methylene groups are incorporated in the chain, and the proportionate effect of the 2-methyl group steadily diminishes.

Highly symmetrical branched alkanes particularly show the effects of reduced molecular surface area on reducing intermolecular interactions. For example, boiling points differ significantly among these three isomers:  $36 \,^{\circ}$ C for *n*-pentane,  $28 \,^{\circ}$ C for 2-methylbutane (isopentane), and  $9 \,^{\circ}$ C for the very symmetrical molecule 2,2-dimethylpropane (neopentane). The distinction comes from the fact that neopentane has the most compact molecular structure geometrically, while *n*-pentane has the most extended structure. *n*-Pentane molecules have a greater surface area over which interactions among induced dipoles can occur. Hence *n*-pentane displays the highest boiling point. Molecules like neopentane can be thought of as presenting a nearly spherical surface to their neighbors. For shapes enclosing similar masses, a sphere has the smallest surface area of any solid.

Rapid proliferation of the number of isomers with increasing number of carbon atoms makes it difficult to generalize further. For a series of isomers, the compound having the most highly branched structure is generally the most volatile. For alkane isomers, the boiling temperatures vary as *n*-alkanes > isoalkanes > highly branched alkanes. This relationship can be seen in the data in Table 9.2, which compares the five isomers of hexane.

Compared with the corresponding *n*-alkanes, cycloalkanes have higher boiling points (Figure 9.4). Given a very small advantage in molecular weight for the *n*-alkanes (2 Da), the differences shown in Figure 9.4 must reflect increased London-force interactions in

**Table 9.2** Normal boiling points of the five isomers of hexane. The highly symmetrical 2,2-dimethylbutane is noteworthy for having a much lower boiling point than the others.

Compound	Boiling point, °C
<i>n</i> -hexane	69
3-methylpentane	63
2-methylpentane	60
2,3-dimethylbutane	58
2,2-dimethylbutane	50

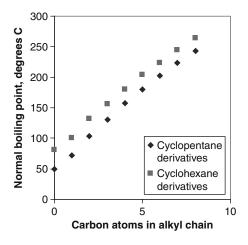


Figure 9.5 Normal boiling points of *n*-alkylcycloalkanes as a function of the number of carbon atoms in the alkyl chain.

the cycloalkanes. If polarizability occurs across the entire surface of the cycloalkane molecule, the disk-shaped cycloalkane will experience greater London-force interactions than the nominally cylindrical molecule of the *n*-alkane.

The monocyclic cycloalkanes of interest in fuel chemistry are cyclopentanes, cyclohexanes, and their derivatives. Consideration of alkylcycloalkanes gets once more into a situation of large numbers of potential isomers, including multiple alkylation of the ring structure and the possibility of branching in the alkyl chain. Alkylcycloalkanes have molecular weights and boiling points higher than those of the parent cycloalkanes. Figure 9.5 illustrates this. The increase in boiling point with increasing length of the alkyl chain shows the expected effect of molecular weight. In fact, beyond the methylderivatives, the effect seems entirely one of molecular weight, because the boiling point of an *n*-alkylcyclopentane differs by  $\pm 1^{\circ}$  from the cyclohexane derivative with one fewer carbon atom in the chain. For example, ethylcyclohexane and *n*-propylcyclopentane have the same molecular formula, C<sub>8</sub>H<sub>16</sub>, with boiling points of 132 °C and 131 °C, respectively.

Multicyclic cycloalkanes also have higher boiling points than the corresponding *n*-alkane. Decahydronaphthalene (usually known by its common name, decalin) occurs as two isomers:

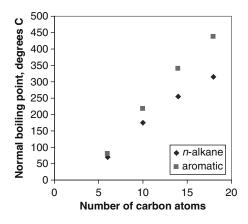
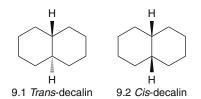


Figure 9.6 Comparison of the boiling points of benzene, naphthalene, anthracene, and naphthacene with the corresponding *n*-alkanes of the same number of carbon atoms.

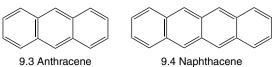


The *trans*- isomer, (9.1), boils at  $187 \,^{\circ}$ C; the *cis*- (9.2), at 196  $^{\circ}$ C. In comparison, *n*-decane has a boiling point of 174 °C.

A carbon–carbon double bond or triple bond has relatively little effect on boiling points compared to the corresponding alkane. The boiling point of an alkene is usually within a few degrees of that of the alkane having the same number of carbon atoms and same chain branching. This can be said of alkynes, though compounds in this family have little importance in fuel chemistry [E].

An important factor in determining the magnitude of London forces is the relative polarizability of the electrons in the molecules involved, i.e. the ability of the electrons to respond to the changing temporary dipole moments of neighboring molecules. Conjugated systems are particularly susceptible to polarization, because of the ability of the participating electrons to delocalize over the system. Aromatic compounds, having an extensive  $\pi$ -bonding system for electron delocalization, can display significant intermolecular interactions, sometimes called  $\pi$ - $\pi$  interactions.

Aromatic compounds have substantially higher boiling points than the *n*-alkanes of the same number of carbon atoms. Figure 9.6 shows this for the series benzene, naphthalene, anthracene (9.3), and naphthacene (9.4).



Heteroatomic compound	Dipole moment, debyes	Boiling point, °C	Related hydrocarbon	Boiling point, °C
Diethyl ether	1.10	34	Pentane	36
Tetrahydrofuran	1.75	65	Cyclopentane	49
Pyridine	2.22	115	Benzene	80
Acetone	3.92	56	Isobutane	-12

**Table 9.3** The effect of polarity on raising the boiling points of selected heteroatomic compounds relative to the analogous hydrocarbons. The hydrocarbons have dipole moments of zero.

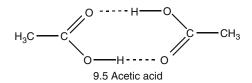
Molecular weights of the aromatic compounds are lower than those of alkanes having the same number of carbon atoms, so the higher boiling points reflect the importance of enhanced intermolecular interactions due to the polarizability of the aromatic systems (i.e. the  $\pi$ - $\pi$  interactions). Figure 9.6 shows that the increase in boiling temperature of the aromatic compound relative to the alkane grows as the number of fused rings increases, indicating a steady enhancement of these interactions. The culmination of ring condensation in an aromatic system is graphite, which has a boiling point estimated to be  $\approx 3800$  °C.

As with alkylcycloalkanes, alkyl derivatives of aromatic compounds offer a remarkable variety of possible isomeric structures. For the *n*-alkylbenzenes, the same trend in variation of boiling point with the length of the alkyl side chain occurs as for the *n*-alkylcyclohexanes. In fact, for most of the compounds in these two families, the boiling points differ by at most a few degrees. As examples, *n*-butylbenzene boils at 183 °C and *n*-butylcyclohexane at 180 °C; *n*-octylbenzene and *n*-octylcyclohexane have the same boiling point, 264 °C.

As a rule of thumb, for a family of hydrocarbon molecules of the same number of carbon atoms, boiling points vary as aromatic > cycloalkane > linear alkane >isoalkane > highly branched alkane. Introduction of a heteroatom (nitrogen, oxygen, or sulfur) into any of these compound classes offers the possibility of creating a permanent dipole moment in the molecule. Boiling points tend to be higher for molecules with permanent dipole moments (dipole-dipole interactions) than for molecules having only induced dipoles, because of the stronger attraction between the oppositely charged ends of the dipoles and those in neighboring molecules. Possible comparisons (having molecular weights differing by  $\leq 2$  Da) include tetrahydrofuran with cyclopentane, where the boiling points are 65 °C and 49 °C, respectively, or pyridine with benzene, where the polar pyridine has a boiling point 35 °C higher than that of non-polar benzene ( $115 \,^{\circ}$ C vs.  $80 \,^{\circ}$ C, respectively). When the heteroatom is in a structure providing strong polarity, the difference is even more dramatic. As an example, acetone boils at 56°C, whereas the non-polar isobutane (having identical molecular weight) boils at -12 °C. In contrast, linear ethers (e.g. diethyl ether) have boiling points roughly comparable with those of the *n*-alkanes of the same molecular weight because of their relatively low dipole moments. Table 9.3 summarizes these comparisons [F].

Situations involving hydrogen bonding present the most marked effects of heteroatoms. A hydrogen atom covalently bonded to a nitrogen or oxygen atom is capable of strong interactions with a non-bonding electron pair on a heteroatom [G]. Hydrogen bonds have a significant impact on physical properties. Methane and water compounds have nearly identical molecular weights, 16 vs. 18 Da, respectively, yet their boiling points differ by  $269 \,^{\circ}$ C (-169 vs. 100  $^{\circ}$ C, respectively) [H]. Alcohols have much higher boiling points than the comparable alkanes or the related ethers, because molecules of alcohols can interact through hydrogen bonding while those of alkanes and ethers cannot. Thus ethanol has a higher boiling point (78  $^{\circ}$ C) than dimethyl ether (-25  $^{\circ}$ C), even though the two compounds have the same molecular weight. Phenols resemble aliphatic alcohols in the sense of being able to form strong intermolecular hydrogen bonds. Hence phenols also have higher boiling points than hydrocarbons of the same molecular weight.

Carboxylic acids are not important as components of fuels, but can be intermediates in fuel production, as is the case with biodiesel. Carboxylic acids can form strong hydrogen bonds with each other and, as would be expected, generally have high boiling points. As neat liquids and even in the vapor phase, carboxylic acids exist largely as hydrogen-bonded dimers, e.g. the acetic acid dimer (9.5).

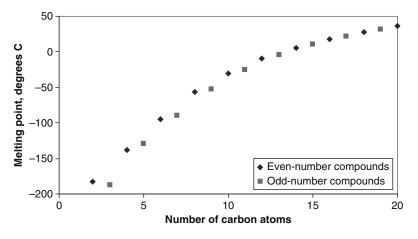


In these dimers, each O-H…O interaction is  $\approx 25-34$  kJ/mol.

Tertiary amines generally boil at lower temperatures than primary and secondary amines of about the same molecular weight, because the tertiary amines lack the ability to engage in hydrogen bonding. Amines form weaker hydrogen bonds than alcohols, and have boiling points lower than those of the corresponding alcohol. In general, boiling points of amines are higher than the corresponding alkanes, but lower than the related alcohols. Primary and secondary amines form hydrogen bonds, and consequently have higher boiling points than related ethers.

Thiols have lower boiling points than alcohols of comparable molecular weight, which can be accounted for by the fact that thiols form much weaker hydrogen bonds, because of the small electronegativity difference between sulfur and hydrogen. But, incorporating a sulfur atom raises the boiling point of an otherwise structurally similar compound. (These two statements are not contradictory; one compares compounds of nearly identical molecular mass; the other, compounds of similar structure.) For example, di-n-propyl sulfide, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, has a boiling point of 141 °C, compared with 98 °C for *n*-heptane, CH<sub>3</sub>--CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>2</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub>3</sub>--CH<sub></sub> Two reasons account for this. First, though sulfur has an electronegativity similar to that of carbon or hydrogen (Table 9.1), many sulfur-containing compounds have permanent dipole moments. Dipropyl sulfide, for example, has a dipole moment of about 1.6 D. Intermolecular interactions between permanent dipoles are stronger than those between temporary induced dipoles. In addition, conceptually replacing a methylene group, -CH<sub>2</sub>-, of mass 14 Da with a sulfur atom, -S-, mass 32 Da, increases the molecular mass. Achieving enough kinetic energy to move the sulfur-containing molecule into the vapor phase requires more thermal energy than for the corresponding alkane.

The increased boiling points of sulfur-containing compounds relative to the alkanes have a practical consequence. When petroleum is separated by distillation (discussed in



**Figure 9.7** The variation of melting points of *n*-alkanes as a function of the number of carbon atoms in the molecule. The melting points vary smoothly when the data are plotted as two separate families of compounds, having even or odd numbers of carbon atoms.

Chapter 12), always the first key step in petroleum refining, sulfur-containing compounds tend to accumulate in the higher-boiling fractions.

## 9.3 Melting and freezing

True melting, i.e. as a completely reversible physical change of state, is seldom of interest in fuel chemistry. Freezing, however, has great importance in aspects of the low-temperature performance of liquid fuels.

Melting points of *n*-alkanes increase with molecular weight, but with a bit of complication compared to boiling-point behavior. A plot of melting point vs. number of carbon atoms in the molecule, analogous to Figure 9.2, would show a zig-zag behavior from one alkane to the next, rather than the smooth progression seen for boiling points. But, the melting points plotted separately for the compounds with an odd number of carbon atoms, and then for those with an even number of carbon atoms as two separate families, would show the expected smooth trend (Figure 9.7).

This difference arises from the fact that carbon chains with an even number of atoms can pack more closely in the solid. The closer molecular packing means that the London forces between each molecule and its neighbors are greater, and melting points are, therefore, higher.

As with boiling points, the effect of chain branching on melting points of alkanes is difficult to generalize, because of the large number of possible branched structures. Two special cases relate to the effects of molecular symmetry. First, many branched-chain structures have lower melting points than the related *n*-alkane, because branching interferes with regular molecular packing in the solid. For both even and odd numbers of carbon atoms in the molecule, iso- compounds (i.e. the 2-methylalkanes) melt at temperatures some 20-30 °C lower than the corresponding *n*-alkanes. Second, branching that produces highly symmetrical structures can result in surprisingly high melting points. As an example, 2,2,3,3-tetramethylbutane melts at 101 °C, while the melting

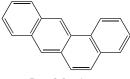
Three-atom chains		Five-atom chains	
Compound	Melting point, °C	Compound	Melting point, °C
Propane	-188	Pentane	-130
Dimethyl ether	-141	Diethyl ether	-116
Ethanol	-114	1-Butanol	-89

Table 9.4 Comparison of the melting points of two sets of structurally related alcohols, ethers, and alkanes.

point of its straight-chain isomer, *n*-octane, is -57 °C, a difference of nearly 160°. While this represents an extreme case, in general symmetrical branched-chain compounds have high melting points, because such structures easily fit together in the solid. Since symmetrical branched-chain compounds also tend to have comparatively low boiling points, because their roughly spherical shape minimizes London-force interactions in the liquid, these two different effects of symmetry – raising the melting point but reducing the boiling point – can result in such compounds having a very narrow temperature range in which they exist as a liquid. As an example, 2,2,3,3-tetramethylbutane boils at 106 °C, only five degrees higher than its melting point.

Cycloalkanes have higher melting points than the related *n*-alkanes of the same number of carbon atoms, but show similar alternation between compounds with even and odd numbers of carbon atoms. These effects derive from the ease (or difficulty) of packing different shapes of molecule into regular solid structures. Both the *n*-alkylcyclopentanes and *n*-alkylcyclohexanes have melting points well below those of the parent cycloalkanes. Also, these compounds have melting points below those of the *n*-alkanes of the same number of carbon atoms. Octylcyclohexane, for instance, has a melting point lower than that of the corresponding parent cyclohexane ( $-20 \,^{\circ}C \,$  vs.  $6 \,^{\circ}C$ , respectively), and than that of the related *n*-alkane (tetradecane, which also melts at  $6 \,^{\circ}C$ ). The molecular shapes of these alkyl derivatives of cyclopentane and cyclohexane are neither fully linear nor completely cyclic and this probably makes it difficult to accommodate these molecules into the structure of a solid.

Most aromatic hydrocarbons have melting points much higher than those of the corresponding aliphatic compounds. As an example, decalin is a free-flowing liquid at room temperature, but naphthalene is a solid, with a melting point of 80 °C. Addition of more rings to the structure drives the melting point up rapidly, e.g. to 216 °C in anthracene and to 438 °C in benz[a]anthracene, (9.6).



9.6 Benz[a]anthracene

The effects at work are those of being able to pack flat, reasonably symmetrical structures into a regular solid, and of the strong intermolecular interactions because of the high polarizability of the delocalized  $\pi$  systems.

Acid	Number of double bonds	Melting point, $^{\circ}C$
Stearic	0	69
Oleic	1	13
Linoleic	2	-7
Linolenic	3	-11

**Table 9.5** The effect on melting point of adding double bonds to the carbon chain for the  $C_{18}$  fatty acids.

Like the related cyclohexane derivatives, *n*-alkylbenzenes have melting points markedly lower than those of the parent, benzene, and lower than the corresponding *n*-alkane of the same carbon number. A methyl group on the benzene molecule, i.e. comparing toluene with benzene, results in a decrease of 100 degrees in melting point  $(-95 \text{ vs } 5^{\circ}\text{C}, \text{ respectively})$  because the methyl group breaks up the easy packing of the hexagonal rings into a solid structure. Even a large molecule such as heptylbenzene melts at -48 °C, compared with the related *n*-alkane of 13 carbon atoms, tridecane, which melts at -5 °C. Effects of molecular symmetry become apparent with multiply substituted alkylbenzenes. For di-substitution, the *para*- isomer usually has a higher melting point than the less symmetrical ortho- and meta- isomers. Among the dimethylbenzenes (xylenes) the variation in melting points follows what might be anticipated from the symmetries of the structures: the least symmetrical isomer, *m*-xylene, melts at -48 °C, while the *p*-xylene has a melting point of 13 °C. This distinction is put to good use in the petrochemical industry, where the more valuable *p*-xylene can be recovered from a mixture of the three isomers by fractional crystallization. More extensively substituted compounds show a similar trend. Thus 1,2,4,5-tetramethylbenzene (durene) melts at a temperature some  $85-100^{\circ}$  higher than the less symmetrical 1,2,3,5- (isodurene) and 1,2,3,4-tetramethylbenzenes (prehnitene) isomers.

The smaller alcohols (i.e. methanol through 1-butanol) have melting points higher than those of the corresponding n-alkanes of about the same molecular weight. This indicates the importance of the hydrogen-bonding interactions among the alcohols. Ethers, which have a permanent dipole moment but lack the capability for hydrogen bonding, fall between the alcohols and the related alkanes (Table 9.4).

The ability of carboxylic acids to form strong hydrogen bonds means that they have relatively high melting points as well as high boiling points. Melting points of the fatty acids increase with increasing chain length. Many naturally occurring fatty acids contain one or more double bonds in the chain, which has the effect of imparting a permanent "kink" in the chain of carbon atoms. The resulting bent chains make it more difficult for molecules to obtain close contact desirable for a crystalline structure. The sequence of fatty acids – stearic, oleic, linoleic, and linolenic acids – provides a good example (Table 9.5).

Sulfur-containing compounds tend to have melting points higher than the related hydrocarbon molecule having the same number of atoms in the main chain, e.g. diethyl sulfide,  $-104 \degree C \ vs. -130 \degree C$  for pentane. This may reflect the slight permanent dipole moment in the sulfur compounds. In comparison with hydrocarbon compounds having approximately the same molecular weight, the sulfur-containing compounds have lower melting points. For example, ethanethiol (62 Da) melts at  $-148 \degree C$ , compared with  $-138 \degree C$  for butane (58 Da).

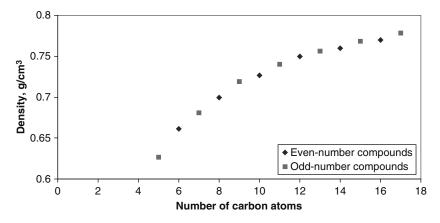


Figure 9.8 Variation in density as a function of number of carbon atoms in the molecule for the *n*-alkanes liquid at room temperature.

## 9.4 Density and API gravity

With increasing number of carbon atoms or  $-CH_2$ - groups in the molecule, the mass of the molecule increases, but because of the ability to adopt various three-dimensional configurations, the volume occupied by the molecule may not increase proportionally. For example, in a typical *n*-alkane, such as decane, a regular alignment of the molecules can be found, if at all, in the solid. In the liquid, additional freedom of motion can result in more disordered molecular configurations, such as coiling, bending, or tangling of the chains of carbon atoms. Because of the closeness of the molecules in the liquid, even in structural configurations that are more random than found in the solid, the intermolecular interactions do not diminish by much. Mass increases more rapidly than volume, an effect seen macroscopically as an increase in density. As with boiling points, the incremental increase in density among the *n*-alkanes lessens with increasing molecular size, because, as molecules get bigger, the percentage change from one molecule to the next is less. A slight effect of even-number vs. odd-number of carbon atoms occurs (Figure 9.8).

Density begins to level off at about  $0.8 \text{ g/cm}^3$ ; in practice all alkanes are less dense than water. Molecules of *n*-alkanes with even numbers of carbon atoms probably pack better, not only allowing for better intermolecular interactions but also providing a reason for the increasing density values.

Specific gravity relates the density of the substance of interest to the density of water at the same temperature. The density of water is  $1 \text{ g/cm}^3$  at  $4 \,^\circ\text{C}$ , so specific gravity and density at this temperature are numerically equal. The distinction lies in the fact that specific gravity is a dimensionless number, whereas density has units of mass per volume. The density of any liquid decreases as temperature increases. For many common liquids the effect of temperature on density is not drastic. However, for the most accurate work the temperature at which the measurement was made must be specified, and comparisons between liquids must be made with data taken at the same temperature. The effect of pressure over the range encountered in practical devices for conversion or utilization of liquid fossil or biofuels is so small that it can usually be ignored.

Particularly in petroleum technology, API gravity (API refers to the American Petroleum Institute) is also used to express liquid density. API gravity is calculated from

API gravity = 
$$(141.5/\text{specific gravity}) - 131.5$$

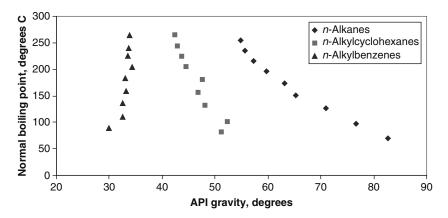
where the specific gravity of the liquid is that relative to water at 15.6 °C (60° F). Since specific gravity is a dimensionless number, API gravity must be so as well. However, API gravity is customarily expressed in units of degrees, e.g. a liquid might be said to be of 29° API gravity. The API gravity scale helps emphasize small differences in density between liquids. For example, two liquids might have specific gravities of 0.84 and 0.88, which would appear to be a small difference. Yet the API gravities of these liquids are 37° and 29°, respectively. API gravity has an inverse relationship to specific gravity, and to density; the higher the API gravity is 10°. Materials with API gravity <10° sink in water; those with API gravity >10° float. Oils having API gravity >31.1° are classified as light oils; 22.3–31.1°, as medium oils; and <22.3°, as heavy oils [I].

Measurement of density, specific gravity, or API gravity is relatively easy and uses equipment much less expensive than used for some of the other tests for characterizing liquid hydrocarbons. As shown later in this chapter, these parameters can also be related to many other liquid characteristics, such as viscosity and sulfur content. Measurement of density or API gravity therefore provides a good indication of the overall quality of the liquid.

Density expresses how many molecules can be packed into a given volume. Packing relates directly to molecular shape. Comparing *n*-hexane and 2-methylpentane (isohexane), packing of the iso-structure into a given volume is less efficient than for the *n*-structure. In the iso-structure, the methyl group that creates the branching sticks out like the proverbial sore thumb. With slightly less efficient packing of the iso-structure, densities are in turn slightly lower, 0.654 for isohexane vs. 0.660 g/cm<sup>3</sup> for *n*-hexane (or 84.9° vs 82.9° API). The large number of possible highly branched alkane structures makes generalizing density relationships among these compounds difficult. Highly symmetrical branched alkanes, such as 2,3-dimethylbutane, can pack efficiently, so have densities higher than the corresponding *n*-alkane. 2,3-Dimethylbutane has a density of 0.668 g/cm<sup>3</sup>, compared to the 0.660 for *n*-hexane (80.3° vs 82.9° API).

Cycloalkanes have higher densities than corresponding alkanes. For example, the density of hexane is  $0.66 \text{ g/cm}^3$  while that of cyclohexane is  $0.78 \text{ g/cm}^3$ . This difference arises from a more efficient filling of a given volume by cyclic structures, which tend to exist in a limited number of molecular configurations, compared to the relatively flexible chain molecules that can adopt a variety of potential configurations. *n*-Alkyl-cyclohexanes and *n*-alkylcyclopentanes have densities greater than those of their respective parent cycloalkanes, and display small increases in density as the length of the alkyl chain increases.

Aromatics have higher densities than corresponding cycloalkanes:  $0.88 \text{ g/cm}^3$  for benzene compared with  $0.78 \text{ g/cm}^3$  for cyclohexane. The benzene structure is completely planar, thanks to the  $sp^2$  hybridization of the carbon atoms, which gives  $120^{\circ}$  C–C bond angles, the exact value of the internal angles of a hexagon. These planar molecules could be even more effective at packing into a given volume than would be the chair or boat forms of cyclohexane. Benzene and the alkylbenzenes are less dense



**Figure 9.9** Relationship between API gravity and boiling point for three families of hydrocarbons of six to fourteen carbon atoms.

than water but more dense than alkanes of about the same molecular weight. For compounds with the same number of carbon atoms, API gravity decreases in the order alkanes > cycloalkanes > aromatics. Among the aromatics, API gravity decreases with increased ring condensation. *n*-Alkylbenzenes have lower densities than benzene itself, probably again because of the difficulty of packing these partially cyclic, partially linear molecules.

Issues of molecular shape also relate to differences in density, up to a point. As an example, densities are  $0.66 \text{ g/cm}^3$  for hexane, 0.78 for cyclohexane, and 0.88 for benzene. This sequence of values suggests that more cyclohexane "dishes" can be packed into a given volume than can the flexible cylinders of hexane, and an even better packing job can be done with the perfectly flat disks of benzene.

Because both API gravity and boiling point relate to the number of carbon atoms in a molecule for various classes of compound, there should also be some relation between API gravity and boiling point. Figure 9.9 illustrates this for *n*-alkanes, *n*-alkylcyclohexanes, and *n*-alkylbenzenes having six to fourteen carbon atoms.

These data suggest that low-gravity liquids are likely to be rich in high-boiling compounds and have a significant contribution of aromatic compounds, whereas high-gravity liquids are most likely to be aliphatic with high concentrations of lowboiling materials.

Heteroatoms can have a significant effect on API gravity. Sulfur is a special concern. Sulfur compounds have dreadful odors, form potential pollutants (the sulfur oxides) during combustion, are mildly corrosive toward metal surfaces, and can poison catalysts (Chapter 13). Because of the effect of sulfur on API gravity, this parameter, an easy measurement to make in the laboratory, can be an estimate of sulfur content. The effect of sulfur can be illustrated by comparing heptane and dipropyl sulfide. Conceptually, they can be considered to be related by the simple replacement of the central methylene group in heptane by a sulfur atom [J]. The C–C bond length is 0.154 nm; the C–S bond length, 0.181 nm. Assuming both molecules to be cylindrical, replacement of  $-CH_2$ – by –S– would increase the volume of the molecule by  $\approx 5\%$ . The difference in atomic mass, 14 vs. 32 Da respectively, means that the molecular

Sulfur compound	API gravity, degrees	Hydrocarbon analog	API gravity, degrees
Benzothiophene	-8.2	Indene	10.6
1-Butanethiol	36.6	Pentane	94.5
2-Butanethiol	39.1	2-Methylbutane	96.7
Butyl ethyl sulfide	37.4	Heptane	76.7
Cyclohexanethiol	13.2	Methylcyclohexane	52.5
Dibenzyl sulfide	2.2	1,3-Diphenylpropane	9.0
Di-tert-butyl sulfide	42.1	2,2,4,4-Tetramethyl-pentane	65.2
Diheptyl sulfide	36.6	Pentadecane	52.6
Diphenyl sulfide	-4.4	Diphenylmethane	9.8
Ethyl isopropyl sulfide	40.1	2-Methylpentane	86.2
1-Heptanethiol	36.4	Octane	71.0
2-Methylbenzenethiol	4.4	o-Xylene	30.1
(Propylthio)benzene	10.1	<i>n</i> -Butylbenzene	33.0
Thiepane	11.3	Cycloheptane	43.2

**Table 9.6** Comparison of API gravities of selected sulfur-containing compounds with those of structurally analogous hydrocarbons.

 
 Table 9.7 Relationship of density and API gravity to dipole moment for a series of oxygen- or nitrogencontaining compounds related to pentane.

Compound	Dipole moment, D	Density, g/cm <sup>3</sup>	API gravity, degrees
Pentane	0	0.626	94.5
Diethylamine	0.92	0.706	69.0
Butylamine	1.0	0.741	59.4
Diethyl ether	1.1	0.714	66.7
1-Butanol	1.66	0.810	43.3

weight of dipropyl sulfide is  $\approx 18\%$  greater than that of heptane. Since mass increases more than volume, sulfur compounds are likely to have higher densities – and lower API gravities – than the corresponding hydrocarbon compounds. This relationship extends, as shown by data in Table 9.6.

Incorporation of nitrogen or oxygen atoms also acts to increase density relative to the hydrocarbon of similar molecular weight. The effect appears to be related to the polarity of the molecules containing heteroatoms, as illustrated by the data in Table 9.7.

Increased polarity may result in decreased intermolecular distances, allowing packing of slightly more molecules per unit volume.

#### 9.5 Viscosity

Viscosity measures resistance to flow. It relates directly to intermolecular interactions, because such forces tend to resist the movement of one molecule relative to another. For a Newtonian fluid [K], in which the shear rate is proportional to the shear stress, viscosity is the constant of proportionality. The unit of viscosity is the pascal-second,

Pa·s. The pascal is  $1 \text{ N/m}^2$ ; if a force of 1 N produces a fluid velocity in the x-direction of 1 m/s for a plane 1 m<sup>2</sup> in area, relative to a second plane 1 m away in the y-direction, the viscosity of the fluid is 1 Pa·s. Viscosity relates to such operations as pumping oil from the well, flow of oil or its products through refinery piping, flow of fuels through fuel lines, and use of liquids for lubrication. The viscosity of all liquids decreases with increasing temperature. As with density data, the temperature(s) at which the viscosity data were obtained should be reported along with the viscosity information itself. For most liquids the temperature dependence of viscosity is much greater than the influence of temperature on density, thus making it more important to pay attention to temperature when considering viscosity behavior.

Because structures are usually drawn on two-dimensional paper, it is possible to lose sight of the fact that hydrocarbon molecules are really three-dimensional. Alkanes are not linear, as implied by CH<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>, but exist in three-dimensional configurations such as 9.7.



9.7 Three-dimensional configuration of pentane

Further, these molecules need not be "linear," even in the zig-zag fashion implied in structure 9.7, but could adopt other configurations involving bends and twists in the chain of carbon atoms. Such configurations can become entangled and, with longer and longer chains, there is increasing opportunity for such entanglement. At the same time, as chain length increases, the surface area of the molecules increases as well, giving enhanced London-force interactions. With an assemblage of such molecules in a confined space – a pipe, for instance – and with a shear stress applied to one end, it is difficult for a system of large, entangled molecules to flow. (An analogy is the problem of trying to push a handful of cooked spaghetti through a pipe.) With smaller molecules, fewer chain entanglements, and fewer intermolecular interactions, it is easier to achieve flow. With the larger molecules the intermolecular interactions are not diminished greatly by molecules flowing past one another. For dodecane, as an example, when a segment of one molecule slips past another molecule, its place is readily filled by a segment of a third dodecane molecule.

For alkanes, viscosity increases with increasing chain length, Figure 9.10.

Branched-chain alkanes have higher viscosity than their straight-chain isomers, a fact that might be counterintuitive, given the lower London-force interactions in the branched-chain compounds. This behavior derives from the greater opportunities for molecular entanglements among branched-chain compounds. Cycloalkanes have viscosities approximately twice as large as those of the comparable open-chain compounds, consistent with the increased London-force interactions in the cyclo- compounds. Benzene has a viscosity slightly lower than that of cyclohexane, suggesting that the completely flat benzene molecules may flow more easily than the cyclohexane rings in the boat or chair configuration. Aromatic compounds with two or more fused rings are solids at ambient temperature.

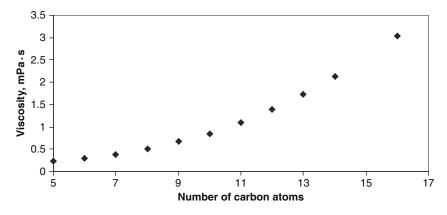


Figure 9.10 Viscosity at  $25^{\circ}$ C of the *n*-alkanes, in mPa·s, as a function of the number of carbon atoms in the molecule.

At identical temperatures, hexane has a viscosity of 0.33 mPa·s, whereas that of cyclohexane is 1.20 mPa·s. This difference can be rationalized by two considerations. First, intermolecular interactions in cyclohexane are larger than in hexane, as shown by the difference in boiling points. Second, molecular hydrodynamics also differ. Molecular motion in liquid hexane involves short, flexible rods moving past each other, while in cyclohexane randomly oriented "dishes" must move. Benzene fits neatly between these two compounds, with a viscosity of 0.65 mPa·s. This might be expected from an increase in intermolecular interaction relative to hexane, but the perfectly flat benzene molecules might move in the liquid more easily than the non-planar cyclohexane molecules.

Heteroatomic compounds have higher viscosities than the related hydrocarbons, indicating an effect of the permanent dipole moment on intermolecular interactions. Replacing a methylene group with a sulfur atom roughly doubles viscosity. For example, at 25 °C the viscosity of cyclopentane is  $0.413 \text{ mPa} \cdot \text{s}$ , but that of tetrahydrothiophene is 0.973 mPa s. When there is an opportunity for hydrogen bonding, viscosity increases greatly relative to the hydrocarbon. For example, the viscosity of *n*-butylamine at 25  $^{\circ}$ C is more than double that of pentane, 0.574 vs. 0.224 mPa·s, respectively. The alcohol functional group has an even more dramatic effect, increasing viscosity by an order of magnitude; for example, *n*-pentyl alcohol has a viscosity of  $3.619 \text{ mPa} \cdot \text{s}$  at  $25 \circ \text{C}$ , but the viscosity of the hydrocarbon with six atoms in the main chain, hexane, is only 0.300 mPa.s. In fats, oils, and the natural waxes viscosity also increases as the carbon chain lengthens. For these compounds the effect of introducing double bonds in the chain must also be considered. Because the "kink" in the carbon chain reduces close contact between the molecules, unsaturated fatty acids have lower viscosities than the related saturated acids. The presence of unsaturation in fatty acids gives fats or oils that contain them a lower viscosity than the comparable fully saturated materials.

Since density, viscosity, and boiling point all depend on molecular size, there must also be relationships between them. These include the dependence of viscosity on API gravity, as shown in Figure 9.11, and the relationship between viscosity and boiling point, Figure 9.12.

Figure 9.11 indicates that low-gravity liquids are likely to have higher viscosities. Furthermore, liquids of high viscosity are likely to have high boiling temperatures.

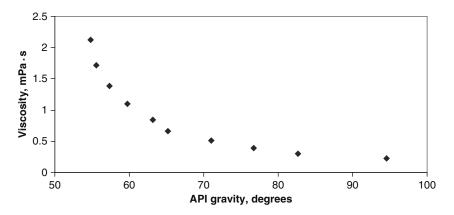


Figure 9.11 The viscosity (mPa·s) at 25°C of *n*-alkanes as a function of API gravity.

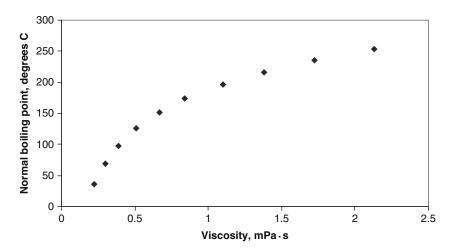


Figure 9.12 The relationship between boiling points of the *n*-alkanes and their viscosities at  $25^{\circ}$ C.

Thus low-gravity liquids tend to be high-boiling, to have high viscosities, and are likely to have significant concentrations of aromatic and sulfur-containing compounds.

#### 9.6 Water solubility

Most hydrocarbons are at best slightly soluble in water. The adage "oil and water don't mix" is a useful first approximation. But, many hydrocarbons dissolve in water to a small extent. Data in Table 9.8 illustrate this.

Generally, aromatic hydrocarbons are more soluble than aliphatic compounds. This may reflect the higher polarizability of the aromatic compounds, and hence a better ability to interact with the highly polar water molecules. Solubility of hydrocarbons in water decreases as molecular size increases. Paraffin wax, for example, which may contain molecules with more than 40 carbon atoms, is totally insoluble.

Compound	Solubility, g compound per kg water
Hexane	$1.6 \times 10^{-2}$
Cyclohexane	$5.5  imes 10^{-2}$
Benzene	$7.5  imes 10^{-1}$
Decane	$2 \times 10^{-5}$
Naphthalene	$3 \times 10^{-2}$

Table 9.8 Solubilities of selected hydrocarbons in water at 25°C.

The situation changes when considering compounds capable of hydrogen bonding with water. Methanol and ethanol are miscible with water in all proportions. 1-Butanol, another alcohol with potential applications as a fuel, dissolves to the extent of about 90 g/kg water. The solubility of alcohols diminishes as molecular size increases, because, as in the case of other physical properties, the "special" portion of the molecule (here, the hydroxyl group) contributes proportionately less and less to the molecular properties as size increases, and at the same time the compound becomes more and more "hydrocarbon-like." The ready miscibility or solubility of the smaller alcohols in water is of concern for their use as fuels, because of the potential of their becoming adulterated with water during handling or storage.

Like their aliphatic counterparts, the smaller phenols are also water-soluble. Phenol itself has a solubility of about 82 g/kg water. Though there seems to be no interest in using phenols directly as fuels, phenols are produced in coal and wood pyrolysis. Any water used in such processes becomes contaminated with phenols (as well as other compounds) and requires processing before being discharged back to the environment.

Ethers do not contain hydrogen atoms that can participate in hydrogen bonding, but can accept hydrogen bonds from water molecules. Consequently, the smaller ether molecules are soluble in water. Dimethyl ether, which has potential as a diesel fuel, dissolves in water to the extent of about 76 g/kg water.

Amines have no direct use as fuels, but some amino- compounds are useful in various fuel processing applications. Like alcohols and phenols, primary and secondary amines form strong hydrogen bonds to each other and to water, and the relatively low molecular weight amines are water-soluble. Tertiary amines cannot form hydrogen bonds to each other, lacking a hydrogen atom bonded to the nitrogen atom, but, like ethers, can form hydrogen bonds to water molecules.

## 9.7 Heat of combustion

Heat of combustion (which commonly means the enthalpy of combustion) indicates the amount of heat released when a unit of fuel – on a molar, or mass, or volume basis – is burned. The terms "calorific value" and "heating value" are often used almost interchangeably with "heat of combustion." In this book, the term *heat of combustion* is used in conjunction with pure compounds, and *calorific value* with fuels that may be mixtures or have ill-defined structures.

Compound	Heat of formation, kJ/mol	Heat of combustion, kJ/mol
<i>n</i> -Octane	-208	-5117
2-Methylheptane	-216	-5110
2,2,4-Trimethylpentane	-224	-5101

Table 9.9 Heats of formation and heats of combustion for selected isomers of octane.

The reported value of heat of combustion depends upon how the combustion process is considered to proceed. That is, two reactions can be envisioned, which can be written generically as

Fuel 
$$+ O_2 \rightarrow H_2O(g) + CO_2(g)$$
,  
Fuel  $+ O_2 \rightarrow H_2O(l) + CO_2(g)$ ,

and which differ by whether the water produced forms as a gas or as a liquid. The latter process liberates more heat, because it includes the heat of condensation of water, i.e.

 $H_2O(g) \rightarrow H_2O(l).$ 

The term higher heating value (HHV) is sometimes used for expressing the heat of combustion with liquid water as a product; water in the vapor phase would give the lower heating value (LHV). For tetradecane as an example (a common component of jet fuels), the higher heating value is -9.39 MJ/mol, and the lower heating value, -8.73 MJ/mol.

A second factor affecting reported heats of combustion, for liquid fuels, is the physical state of the fuel. Data may be reported in some sources for the liquid, or in others for the fuel in its gaseous state. The heat of combustion for the fuel as a gas will be the higher of the two, because in this case the heat of vaporization of the liquid does not have to be accounted for. Using tetradecane again, the heat liberated in the reaction

$$C_{14}H_{30}(g) + 21\frac{1}{2}O_2 \rightarrow 14CO_2 + 15H_2O(g)$$

is -9.46 MJ/mol (i.e. per mole of tetradecane), whereas the corresponding value for

$$C_{14}H_{30}(l) + 21\frac{1}{2}O_2 \rightarrow 14CO_2 + 15H_2O(g)$$

is -9.39 MJ/mol

Since the ultimate purpose of any fuel is to be burned as a source of thermal energy, heat of combustion has a very important role in evaluating, comparing, and selecting among various fuels. The basis on which it is expressed is also critical. In some fuel applications, most notably vehicles and aircraft, the volume of the fuel tanks, not the mass of fuel, usually limits how much fuel can be carried. In such cases, the heat of combustion per unit volume, sometimes called the volumetric energy density, is the important criterion. When volume is not the limiting factor, e.g. in coal stockpiled for combustion in electricity generating plants, heat of combustion per unit mass is more important. Though heat of combustion has great importance as a fuel property, it is by no means the only criterion for assessing the suitability of a fuel for use. Many other physical and chemical properties – sulfur

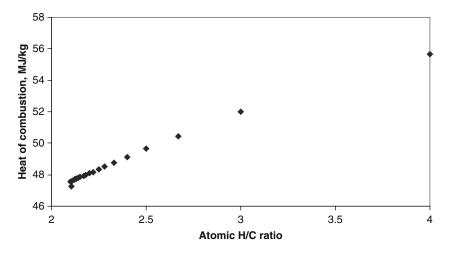


Figure 9.13 Heat of combustion of n-alkanes as a function of atomic H/C ratio. Heats of combustion are for gaseous alkanes producing liquid water.

content, viscosity, ash yield, and stability during storage, to name just a few – must also be taken into account.

Among alkanes, branched-chain compounds are slightly more stable than the corresponding straight-chain isomers; heats of formation of the branched-chain compounds are slightly more exothermic than of the straight-chain compound. Consequently, the heat of combustion of the straight-chain compound is slightly more exothermic; i.e. the straight-chain isomer is a slightly better fuel in this respect. Usually the differences are so small as to be negligible in practice. Data for some of the isomers of octane illustrate this (Table 9.9).

Molar heat of combustion increases with molecular mass among alkanes,  $\approx 650 \text{ kJ}$  for each additional  $-\text{CH}_2$ - group added to the molecule. On a unit mass basis, methane has the highest heat of combustion among the alkanes. Heat of combustion per mass of fuel decreases as molecular size increases, becoming almost constant for molecules larger than octane. On a mass basis the elements themselves have a heat of combustion of -142 MJ/kg for hydrogen, and -34 MJ/kg for carbon. Compounds of high hydrogen content have a clear advantage when comparing heats of combustion per mass of sample. This leads to a relationship between the heat of combustion and atomic H/C ratio, illustrated for the *n*-alkanes in Figure 9.13.

The heat of combustion on a mass basis becomes nearly constant for compounds larger than octane because the H/C ratio is nearly (but not exactly) constant. Decane,  $C_{10}H_{22}$ , has an H/C ratio of 2.20; tripling the molecular size to triacontane,  $C_{30}H_{62}$ , reduces H/C only to 2.07.

Among alkanes, compounds of low molecular weight also have low density. With larger molecules, their greater density offsets, at least in part, the lower heat of combustion per unit weight. A compound such as hexadecane (cetane),  $C_{16}H_{34}$ , an important component of diesel fuel, has a heat of combustion per gram about 3% lower than that of the lightest liquid alkane, pentane (-47.7 vs. -49.1 MJ/kg, respectively), but a volumetric heat of combustion nearly 20% higher (respectively -36.7 vs. -30.7 MJ/l). Table 9.10 compares the heats of combustion on a weight basis and volumetric basis for

	Heat of combustion		
Compound	Mass basis, MJ/kg	Volumetric basis, MJ/l	
Pentane	-49.1	-30.7	
Hexane	-48.8	-32.2	
Heptane	-48.5	-33.0	
Octane	-48.4	-33.8	
Decane	-48.1	-35.0	
Undecane	-48	-35.5	
Dodecane	-47.9	-35.9	
Tridecane	-47.8	-36.1	
Tetradecane	-47.8	-36.3	
Pentadecane	-47.8	-36.7	
Hexadecane	-47.7	-36.7	
Heptadecane	-47.7	-37.1	

**Table 9.10** Heats of combustion for selected *n*-alkanes, on mass and volume basis. Data are for the gaseous alkane and production of liquid water.

selected *n*-alkanes. Where fuel volume is limiting, higher alkanes would be preferable, because of their higher volumetric heat of combustion, to smaller compounds. Of course, other factors also are important in fuel selection for specific purposes, such as ignition and combustion characteristics, volatility, and resistance to freezing.

Cycloalkanes have slightly lower heats of combustion than alkanes of the same number of carbon atoms. For instance, the heat of combustion is -4144 kJ/mol for hexane but only -3926 for cyclohexane. This trend follows the rule of H/C ratio discussed earlier, the values being 2.33 for hexane and 2.00 for cyclohexane. Because of density differences, the greater density of cycloalkanes provides a higher heat of combustion per unit volume. For hexane and cyclohexane, the volumetric heats of combustion are -31.8 MJ/l and -36.4 MJ/l, respectively. In airplanes, fuels rich in cycloalkanes – so-called naphthenic fuels – provide greater operational range, because a greater amount of chemical energy can be obtained from a given volume of fuel.

Cyclopentane, cyclohexane, and their alkyl derivatives all have nearly identical heats of combustion on a mass basis, about -11.2 to -11.3 MJ/kg. Because the densities of these compounds increase as the alkyl side chain gets larger, their volumetric heats of combustion slowly increase with the size of the alkyl chain.

Heats of combustion of aromatics are much lower than those of the corresponding cycloalkanes, e.g. -3.27 MJ/mol for benzene vs. -3.93 MJ/mol for cyclohexane. Part of the reason comes from benzene having a much lower H/C ratio than cyclohexane, but the resonance stabilization energy of benzene also has a significant role. Resonance stabilization of benzene (and other aromatic compounds) is usually discussed in the context of heats of hydrogenation, e.g. the reaction

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}.$$

From the heats of hydrogenation of cyclohexene and cyclohexadiene one can extrapolate [L] an expected heat of hydrogenation for the hypothetical compound cyclohexatriene. In fact, the measured heat of hydrogenation of benzene is lower than this extrapolated value by about 150 kJ/mol. That is, benzene is more stable,

by 150 kJ/mol, than would be expected from this line of reasoning. It is a lot easier to burn benzene than to hydrogenate it; but in combustion too (indeed in any reaction that must overcome the resonance stabilization) there is an energy "penalty" that derives from the special stability associated with aromatic molecules.

Heats of combustion of alkylbenzenes, on a mass basis, slowly increase with increasing length of the side chain because, as more methylene groups are incorporated in the chain, the H/C ratio increases. Volumetric heats of combustion slowly increase as well.

Heteroatoms decrease the heat of combustion relative to the hydrocarbon having the same number of main atoms (e.g. comparing ethanol with propane or methylamine with ethane). Oxygen atoms add nothing to the heat of combustion; consequently, heats of combustion can be reduced greatly relative to the hydrocarbon molecule. The effect is more pronounced in small molecules, because the heteroatom has a proportionately greater effect on the composition and molecular weight of the compound. On a molar basis, the heat of combustion of ethanol is 38% less than that of propane; diethyl ether, 22% less than that of pentane. Sulfur contributes to the heat of combustion, so the decrease for sulfur-containing compounds, relative to the parent hydrocarbon, is not so great as for the comparable oxygen compound. As an example, the heat of combustion of propane is -2058 kJ/mol. For dimethyl ether, the value drops to -1460 kJ/mol; however, for dimethyl sulfide the heat of combustion is -1904 kJ/mol, not much lower than the parent compound. Heteroatoms bring other problems as well, particularly formation of nitrogen or sulfur oxides during combustion; these compounds require some type of post-combustion clean-up to avoid their being emitted to the environment.

# 9.8 The special effects of aromaticity

To this point, it would seem that considerations of intermolecular interactions, surface area, and molecular shape provide a convenient and consistent way of relating the properties of alkane, cycloalkane, and aromatic molecules. Comparisons between hexane, cyclohexane, and benzene have been discussed in previous sections. Unfortunately, the story breaks down almost immediately when pushed beyond benzene. The next member of the aromatic family is the two-ring compound naphthalene,  $C_{10}H_8$ . The related two-ring cycloalkane is decalin. The ten-carbon-atom alkane is decane. The argument previously established for the effect of molecular shape on density works as might be expected. The respective densities of the three compounds are 0.73 for decane, 0.90 for decalin, and 1.14 g/cm<sup>3</sup> for naphthalene. Consideration of boiling points based on the foregoing argument leads to the expectation that the sequence of values should be decane < decalin  $\approx$  naphthalene. The actual boiling points support this, but only partially. The values are  $174 \,^{\circ}$ C for decane, 194 °C for decalin (as might be expected), but 218 °C for naphthalene, a good bit higher than might have been predicted. This suggests that other factors are active in the naphthalene case, a suggestion reinforced by the fact that decane and decalin are free-flowing liquids at room temperature, whereas naphthalene is a solid (melting point of 80 °C). Some factor in addition to London-force or van der Waals interactions must be involved. This other factor is considered to be interactions

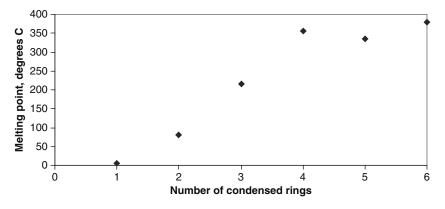
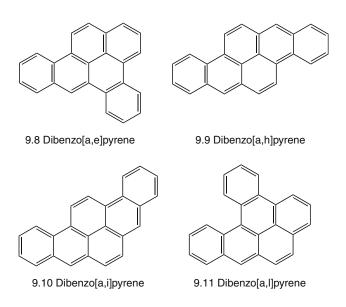


Figure 9.14 Variation of melting point with number of fused rings for benzene and linear cata-condensed compounds through hexacene. Data for pentacene are not well established.

between the highly polarizable  $\pi$  clouds on the aromatic ring systems, the so-called  $\pi$ - $\pi$  interactions. Because of the easy polarizability of the delocalized  $\pi$  electrons,  $\pi$ - $\pi$  interactions are stronger than the temporary induced dipoles associated with London-force interactions in alkanes, but not as strong as hydrogen bonds or covalent bonds.

Increasing the number of fused rings in the aromatic structure also increases  $\pi-\pi$  interactions. Increasing melting points and decreasing solubility reflect this. Polycyclic aromatic hydrocarbons having three or more fused rings can exist as more than one structural isomer. As the compounds in this family get larger, the number of possible isomers increases, though not at so dramatic a rate as in the alkanes. The dibenzopyrenes (9.8 through 9.11) provide an example:



Just as with aliphatic compounds, molecular shape affects the ability to pack into regular structures in the solid state, and thus affects intermolecular interactions that govern such behavior as melting point and solubility. Consequently, there is not a single, comprehensive relationship between number of fused rings and melting point or solubility. As a generality, however, melting points increase and solubilities decrease as the number of fused rings increases. However, when attention is confined to a single structural family, such as the cata-condensed [M] compounds from naphthalene to hexacene, regular trends are found (Figure 9.14).

#### Notes

- [A] A second factor is also in play. Each polarized bond can be thought of as a vector, and the dipole of the molecule as being the resultant of all the individual vectors. In highly symmetrical molecules, the net dipole can be zero even if each of the bonds is highly polarized. The tetrahedral carbon tetrachloride molecule provides a classic example; it has a dipole moment of zero despite the difference in electronegativity between carbon and chlorine (2.5 vs. 3.0, respectively).
- [B] Johannes van der Waals (1837–1923, Nobel Prize in Physics, 1910) contributed greatly to science in the late nineteenth and early twentieth centuries. His landmark Ph.D. thesis established an equation of state that covered both the gaseous and liquid states. Establishing relationships between the pressure, volume, and temperature of liquids and gases required taking account of the existence of the intermolecular forces which are now named for him. van der Waals' many other contributions included establishing the law of corresponding states, a theory of capillarity, and a theory of binary solutions. van der Waals' Ph.D. thesis is still in print (as a Phoenix edition from Dover Publications), a claim not many of us can make.
- [C] These forces have nothing to do with the city; they are named in honor of the physicist Fritz London (1900–1954). London was born, educated, and spent his early career in Germany. He left in 1933, when Hitler came to power and the Nazi regime began enacting its poisonous brew of racial, anti-Semitic laws. After periods in England and France, London eventually settled at Duke University in the United States, where he spent the remainder of his life. In addition to his contributions to the field of chemical bonding and intermolecular interactions, he also helped develop understanding of superconductivity (with his brother Heinz) and of superfluidity.
- [D] It is important to remember that any substance boils when its vapor pressure becomes equal to the prevailing pressure, i.e. boiling points are highly dependent upon the pressure at which they are measured. Throughout this chapter and the remainder of the book, boiling point data are always given as the normal boiling point, i.e. the boiling point at 101.3 kPa (1 atmosphere pressure), *unless specifically stated to the contrary in the text*.
- [E] The lone exception is acetylene,  $C_2H_2$ , the simplest of the alkynes. Acetylene is a useful fuel gas, for example as used in welding torches. Acetylene is commonly made from reaction of calcium carbide with water:  $CaC_2 + 2 H_2O \rightarrow Ca(OH)_2 + C_2H_2$ . In turn, calcium carbide comes from reaction of the oxide with carbon, where anthracites provide a relatively inexpensive source of the carbon:  $CaO + 3 C \rightarrow CaC_2 + CO$ . In the early decades of the twentieth century, prior to the ready availability of cheap petroleum (and the ethylene made from it), acetylene was a crucial feedstock for the organic chemical industry.

- [F] The debye is the unit commonly used to express dipole moments, though it is not an SI unit. The SI unit, which is way too big for practical use, is the coulomb-meter; the conversion is that 1 debye =  $3.336 \times 10^{-30}$  coulomb-meter.
- [G] There is evidence that water, and possibly other molecules capable of forming hydrogen bonds, can so bond to aromatic molecules under some conditions. Presumably the hydrogen atom covalently bonded to oxygen can interact with the  $\pi$ -electron system of the aromatic molecule, somewhat as it does with non-bonding electron pairs. Whether or not hydrogen bonding to aromatic systems is important in fuel chemistry is not well understood.
- [H] The hydrogen bonding interaction responsible for water being a condensed phase at ambient conditions is of extreme importance to us. Virtually all life forms on our planet need, or actually live in, liquid water. Without hydrogen bonding, water would certainly be a gas at ordinary temperatures and pressures, probably boiling somewhere around -150 °C. The origin (even if it could have occurred) and subsequent evolution of life would have been much, much different.
- [I] Various organizations might use slightly different values of gravity for making these classifications, but the differences are not extreme. Also, sometimes oils of  $<10^{\circ}$  are classified as extra-heavy oils.
- [J] This does not mean that dipropyl sulfide can be synthesized by a simple chemical version of "cut and paste," in which the central methylene carbon is removed and a sulfur atom neatly slipped into the molecule in its place. Various synthetic routes to sulfides are available; as an example, one could start with a thiol, e.g. propanethiol, form the anion by reacting with base, and then react the anion with an appropriate alkyl halide.
- [K] Most simple hydrocarbons and their heteroatomic derivatives are Newtonian fluids. Heavy crude oils, tars, and similar complex mixtures of high-molecularweight compounds are non-Newtonian liquids with more complicated viscosity behavior. For discussion of pure compounds given in this chapter, the assumption of Newtonian behavior is reasonable.
- [L] This result also provides a wonderful example of the dangers of extrapolation of data. The most eloquent warning of the problems that can arise from doing this has been given by Mark Twain in *Life on the Mississippi* (referenced below).
- [M] Polycyclic aromatic hydrocarbons are referred to as being cata-condensed if any given carbon atom is shared by no more than two rings. Examples include anthracene and phenanthrene. The term peri-condensed denotes compounds in which a carbon atom might be shared between more than two rings, as in pyrene.

#### Reference

 Pauling, L. *The Nature of the Chemical Bond*. Cornell University Press: Ithaca, 1960; Chapter 3. (Might as well go straight to the fount.)

#### **Recommended reading**

Harvey, R.G. *Polycyclic Aromatic Hydrocarbons*. Wiley-VCH: New York, 1997. Unfortunately, most introductory textbooks of organic chemistry seldom mention aromatic hydrocarbons larger than naphthalene (or sometimes even larger than benzene). This monograph is a useful source of information on a large number of compounds of this kind.

- Lide, D.R. *Handbook of Chemistry and Physics*. CRC Press: Boca Raton, FL, 2009. There are many useful compilations, in print and on the web, of data on the physical and thermo-chemical properties of hydrocarbons and the related heteroatomic compounds. This book in particular is an excellent resource.
- Reid, R.C., Prausnitz, J.M., and Poling, B.E. *The Properties of Gases and Liquids*. McGraw-Hill: New York, 1987. This book is an excellent source of methods for calculating or estimating properties of liquids from fundamental information. It treats many of the properties discussed in this chapter, and a great many more besides.
- Smith, M.B. and March, J. *March's Advanced Organic Chemistry*. Wiley: Hoboken, NJ, 2007. Chapter 3 provides an in-depth discussion of weak interactions such as hydrogen bonding and  $\pi$ - $\pi$  interactions, with numerous references to the primary literature.
- Szmant, H. Harry. *Organic Chemistry*. Prentice-Hall: Englewood Cliffs, NJ, 1957. Though this is now a rather elderly textbook, Chapter 24 provides a good discussion of the physical properties of organic compounds, much more so than many modern introductory organic texts.
- Twain, M. Life on the Mississippi. Numerous editions of this classic are available. In Chapter XVII, Twain extrapolates data accumulated over 176 years to "prove" that the Mississippi River must once have been 1300000 miles long. This chapter should be required reading for all scientists and engineers.

# **10** Composition, properties, and processing of natural gas

Natural gas is a mixture of hydrocarbons with various quantities of non-hydrocarbons, which exists either in the gas phase or in solution with petroleum in natural underground reservoirs. The principal hydrocarbon component is methane. In most parts of the world, by the time the gas has been treated and distributed to consumers, it consists almost entirely of methane.

Gas produced during catagenesis usually migrates through porous rocks in the Earth's crust until it encounters a formation of non-porous rock. This non-porous rock prevents further migration of the gas, effectively trapping it in the porous rock below. The porous rock becomes a reservoir for the gas. The gas can be classified according to how it is found. Associated gas is found in conjunction with accumulated oil, either dissolved in the oil, called dissolved gas, or as a separate gaseous phase above the oil, gas-cap gas. Non-associated gas is found without accompanying oil. A reservoir of non-associated gas could arise from gas migrating to a different location than that to which oil migrated, or from formation of gas in the gas window, i.e. without oil. About 60% of the world's natural gas is non-associated.

Other sources of methane-rich gases occur in nature. Biogenic gas, produced during diagenesis, comes from the action of anaerobic bacteria on accumulated organic matter. Landfill gas is produced in the same way, but differs in that the feedstock is the organic residues of civilization, accumulated as solid waste in landfills. Excrement from humans or other animals also reacts in the same way, providing a useful source of fuel for farms or even domestic use [A]. Methane forms and accumulates in coal seams; its deliberate removal prior to mining provides another source, coalbed methane.

Two other methane sources may offer enormous reserves of fuel. Shale gas is produced in shales (laminated, compacted sediments of clay or silt) that were rich in kerogen and that have experienced catagenesis conditions typical of the oil window. Unlike conventional oil source rocks, the shales have so little permeability that gas does not migrate, but remains adsorbed in the pores and natural fractures of the shale. Many countries around the world have shales that are either already sources of gas, or potential sources in the future. A very different, but also unconventional, source lies on the sea floor or in the tundras of the far North. At low temperatures, water molecules associate in cage-like structures large enough to accommodate small molecules in their interior. Methane can be trapped in this way. The generic structures are known as clathrate hydrates; when methane is the entrapped molecule, they are called natural gas hydrates or methane hydrates [B]. Optimistic estimates suggest that possibly 2500 Gt of methane is trapped in hydrates on the sea floor, and another 500 Gt in hydrates in the permafrost in northern tundras. This amount exceeds by an order of magnitude all the other known natural gas reserves [C]. World consumption of natural gas in 2007 was about 2.7 Gt.

Compound	Normal boiling point, $^{\circ}C$	
Methane	-162	
Ethane	-88	
Ethylene	-104	
Propane	-42	
Propene	48	
Butane	-0.5	
1-Butene	-6	
Pentane	36	
1-Pentene	30	
Hexane	69	
1-Hexene	63	

**Table 10.1** Normal boiling points of the *n*-alkanes and 1-alkenes up to C<sub>6</sub>.

Depending on where in the oil or gas window a particular natural gas formed, it might contain other light alkanes and alkenes. Thermal cracking during catagenesis gives rise to a variety of other gaseous products in addition to methane. Two types of natural gas can be found: one in which methane is essentially the only hydrocarbon component, and one that contains not only methane but other small alkanes and alkenes. As discussed in the next section, there are significant differences in boiling point among these small hydrocarbons (Table 10.1).

These volatility differences make it relatively easy to condense components heavier than methane. Gases can be classified as dry gas, essentially pure methane, and wet gas, for which the condensable hydrocarbons amount to greater than 0.040 1/m<sup>3</sup>. In this context, the terms wet and dry have nothing to do with water - they refer only to the presence or absence of condensable hydrocarbons. Hydrocarbons recovered from wet gas can be separated by processes that are discussed later in this chapter, and themselves represent useful materials. Ethane is converted to ethylene, the most important feedstock for the petrochemical industry. Propane and butane are useful fuel gases in their own right, propane being the principal component of LPG, liquefied petroleum gas.

Condensable hydrocarbons that are liquid at ambient temperature make up natural gasoline (sometimes also known as casinghead gasoline, or as pentanes-plus), which can be used as a petrochemical feedstock or blended with other gasoline sources in a refinery. The composition of natural gasoline varies from one source to another. Generally it consists of pentane and larger hydrocarbons, though some samples can contain appreciable amounts (i.e. a few tens of percent) of butane.

Some natural gas deposits contain hydrogen sulfide, usually in small amounts [D]. Such gas is known as sour gas. Hydrogen sulfide can arise in several ways. Some amino acids contain the thiol group, e.g. cysteine, HSCH<sub>2</sub>CH(NH<sub>2</sub>)COOH. Anaerobic decay of proteins containing such amino acids liberates  $H_2S$ . The sulfate ion, second only to chloride in concentration of anions in saline waters, undergoes anaerobic microbial reduction, e.g.

$$3 \text{ SO}_4^{-2} + \text{C}_6 \text{H}_{12} \text{O}_6 \rightarrow 6 \text{ HCO}_3^- + 3 \text{ H}_2 \text{S}.$$

If sulfur, regardless of source, survives diagenesis it can be incorporated into various organic compounds in kerogen. Then, thermal decomposition of sulfur-containing compounds could occur during catagenesis. Sulfur occurs in organic compounds in many kinds of functional group; however, the C–S bond has a lower dissociation energy than the C–O bond, so these groups are likely to be lost, possibly via reactions analogous to those discussed in Chapter 8 for oxygen functional groups. As an example, thermally induced desulfurization of a thiol can be represented as

## $RCH_2CH_2SH \rightarrow RCH = CH_2 + H_2S.$

Sour gas presents several problems. Hydrogen sulfide itself has a dreadful smell (it is the gas responsible for the characteristic odor of rotten eggs), and, worse, is poisonous. A concentration in air of only 15 parts per million represents the short-term exposure limit, i.e. to which exposure for fifteen minutes could lead to serious health effects. Hydrogen sulfide dissolves in water to form a mildly acidic solution that can corrode metallic components of gas handling and storage systems. Hydrogen sulfide present in the gas when it is burned is converted to the sulfur oxides:

$$\begin{split} & 2\,H_2S+3\,O_2\rightarrow 2\,H_2O+2\,SO_2,\\ & H_2S+2\,O_2\rightarrow H_2O+SO_3. \end{split}$$

Release of these oxides to the atmosphere is followed by their eventually being washed out of the atmosphere, reducing the pH of the precipitation. This results in the serious environmental problem commonly known as acid rain [E]. Processes that remove hydrogen sulfide from natural gas are collectively known as sweetening, and are discussed later in this chapter.

Some natural gas deposits also contain the noble gases, helium being the most important. Natural gas deposits with up to  $\approx 8\%$  helium are known. In the United States, the principal commercial source of helium is the natural gas found in the Texas panhandle, which has  $\approx 2\%$  helium. Other significant sources occur in Algeria and possibly Qatar. Helium derives from radioactive decay of isotopes of uranium, thorium, and radium in the Earth's crust, for example

$$^{238}\text{U}_{92} \rightarrow ^{234}\text{Th}_{90} + {}^{4}\text{He}_{2}.$$

Smaller amounts of the other noble gases can also occur in natural gas, argon and radon [F] being examples. Radon also originates from radioactive decay of uranium, thorium, or radium, e.g.

$$^{226}Ra_{88} \rightarrow ^{222}Rn_{86} + {}^{4}He_2.$$

Helium is recovered by a sequence of cryogenic processes. The natural gas is first cooled sufficiently to condense the hydrocarbons, leaving a mixture of nitrogen and helium in the gaseous state. Further cooling causes the nitrogen to condense. The remaining gas is passed through activated carbon adsorbents at liquid nitrogen temperature, i.e.  $-196^{\circ}$ C.

Hydrogen occurs, albeit rarely, in some natural gas deposits. Its formation with natural gas may be due to dehydrogenation reactions late in catagenesis. Hydrogen is a remarkably mobile material that readily finds its way through any pores, cracks, or other leaks in rock formations (or in process equipment, for that matter). Small amounts of hydrogen that might form can often escape into the atmosphere, where Earth's gravitational field is not adequate to retain it.

Carbon dioxide usually – but not always – is a minor component of natural gas. Carbon dioxide can account for 50% or more of the natural gas in, e.g. Mexico,

Constituent gas	Algeria	Canada (western)	Denmark	Thailand	USA (Penna.)
Methane	83.0	95.2	87.2	72.4	88.2
Ethane	7.2	2.5	6.8	3.5	11.0
Propane	2.3	0.2	3.1	1.1	1.9
Butanes	1.0	0.06	1.0	0.5	0.79
Pentanes	0.3	0.02	0.17	0.1	0.26
Hexanes+	NR	0.01	0.05	0.07	0.11
Helium	0.2	NR	NR	NR	0.10
Hydrogen	NR	Trace	_	NR	0.003
Nitrogen	5.8	1.3	0.3	16.0	3.04
Carbon dioxide	0.2	0.7	1.4	6.3	0.02

**Table 10.2** Examples of natural gas composition (volume percent) from various sources. Data for butanes and pentanes include both n- and iso- compounds; "hexanes+" includes hydrocarbons of C<sub>6</sub> and larger. NR – not reported.

Pakistan, and the North Sea. Several processes account for the production of carbon dioxide, including anaerobic decay reactions:

$$C_6H_{12}O_6 \rightarrow 3 CH_4 + 3 CO_2;$$

decarboxylation reactions:

$$RCH_2CH_2COOH \rightarrow RCH_2CH_3 + CO_2;$$

oxidation of hydrocarbons by oxygen dissolved in surface waters that percolate through the reservoir:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2;$$

and possibly the thermal decomposition of carbonate rocks strongly heated by contact with magma:

$$CaCO_3 \rightarrow CaO + CO_2$$
.

The composition of natural gas as it comes from the well varies quite a bit around the world. Table 10.2 shows the composition of samples of natural gas from different parts of the world.

# 10.1 Gas processing

Several processing or purification steps are usually applied to natural gas before it is put into a pipeline system for sale to consumers. These operations focus on removing those components other than methane: water, hydrogen sulfide, and other hydrocarbon gases. The amount of processing, and the specific processing steps used, depend on the composition of the gas as it comes from the well.

## 10.1.1 Dehydration

Dehydration is usually the first step in gas processing. It is done for several reasons: some of the subsequent processing steps operate below  $0^{\circ}$ C; any water present would freeze to ice while the gas was being treated. Moisture in the gas in the distribution

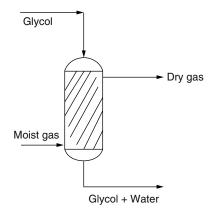


Figure 10.1 A simple process for gas dehydration using one of the glycols as the dehydrating agent.

and storage systems could cause "icing" of valves, gauges, and fuel lines during cold weather. Condensation of vapor to liquid water can accelerate corrosion, because hydrogen sulfide and carbon dioxide dissolve into the liquid to produce mildly acidic solutions.

Water vapor can be removed by absorbing it into liquids, or adsorbing it onto the surfaces of solids. Both approaches have merit, and both are used commercially. Gas dehydrators are tanks or towers in which the gas is brought into contact, usually in countercurrent flow, with compounds that absorb moisture. Such compounds include diethylene glycol, HOCH<sub>2</sub>CH<sub>2</sub>OH<sub>2</sub>CH<sub>2</sub>OH; triethylene glycol, HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub> CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH; or tetraethylene glycol, HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH. Of these, triethylene glycol is the dominant choice, though the others certainly work well. Use of the glycols relies on two properties: first, the abundance of oxygen atoms in these molecules provides numerous sites for absorbing and retaining water molecules via hydrogen bonding. Hydrogen atoms in the hydroxyl groups at the ends of the molecules can hydrogen bond to water molecules, while the oxygen atoms in the ether groups in the interior of the molecules can accept hydrogen bonds from water molecules. Second, these glycols have very low vapor pressure. This means that the gas stream, during treatment, is not contaminated with a new impurity (i.e. glycol vapors) while the moisture is being removed.

Figure 10.1 presents a flow diagram of a dehydration process. Gas containing moisture is brought into contact with the dehydrating agent in a countercurrent flow absorber. Water is transferred into the dehydrating agent, producing the desired stream of dried gas, along with a solution of water in, say, triethylene glycol. Economy of operation requires that the glycol be recovered and recycled. Options for regenerating the glycol include treating it in vacuum to draw water off as a vapor for subsequent condensation, or stripping the glycol by passing through it some vapor that will not react with glycol under these conditions.

The alternative approach relies on the adsorption of water vapor onto the surface of solids. In this application, adsorption results from van der Waals interactions of water molecules with the surface of the adsorbent (also called the desiccant). The use of solids is preferred in two specific cases. One is in relatively small-scale applications, where the

simplicity and ease of operation, as described below, are advantageous. The other is when essentially complete dehydration of the gas is required.

Several kinds of solid can be used in this application, including silica gel, activated alumina, activated bauxite, and molecular sieves. Silica gel is a colloidal form of silicon dioxide, which, because of its high surface area per unit mass, finds many applications as a dehydrating agent. Many electronic and optical goods come with a small packet of silica gel in the packaging, to prevent water vapor from condensing on the items during shipping and storage. Activated alumina is a granular form of aluminum oxide having high porosity, so this also has a high surface area available for adsorption. Activated bauxite is similar, but has other constituents in addition to the aluminum oxide, such as iron oxide or clays. (Bauxite is better known as the ore that is the principal source of aluminum.) Molecular sieves are natural or synthetic zeolite minerals [G] having pore sizes small enough to allow certain molecules to enter or pass through the solid, while excluding molecules of larger size; in this regard they operate on a molecular level analogously to an ordinary sieve used to separate particles of different size, such as rocks from sand.

The simplest adsorption system would involve a vessel containing a bed of adsorbent, with provision for the gas to pass through the bed. A point is reached at which the adsorbent has taken up so much water that it has reached the limit of its capacity, and must be regenerated before it can be used further. Regeneration can be accomplished with a flow of hot gas through the bed. A more practical system would use two vessels in parallel, so that one can be in use adsorbing water while the other is being regenerated.

## 10.1.2 Gas sweetening

The several negative characteristics of hydrogen sulfide make sweetening the most important single process in gas treatment. Not surprisingly, numerous approaches have been developed.

Useful absorbents for hydrogen sulfide come from the family of alkanolamines. The simplest is monoethanolamine (MEA), HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>. These compounds contain both alcohol and amine functional groups. Other compounds in this family suitable for sweetening include diethanolamine (DEA), (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH, and diisopropylamine (DIPA), ((CH<sub>3</sub>)<sub>2</sub>CH)<sub>2</sub>NH. Sweetening operations using these reagents rely on the fact that, as a weak acid, hydrogen sulfide can be absorbed and retained by bases. As with dehydration, removal of one impurity, i.e. H<sub>2</sub>S, should not add a new one to the gas stream. Thus reagents for sweetening should be mild bases with low vapor pressures, specifications which diethanolamine meets well:

 $(HOCH_2CH_2)_2NH + H_2S \rightarrow (HOCH_2CH_2)_2NH_2^+ + HS^-.$ 

Figure 10.2 illustrates the process flow scheme for sweetening with alkanolamines. Sour gas contacts the alkanolamine in countercurrent flow. The alkanolamine–hydrogen sulfide solution, referred to as the "rich" solution, proceeds to a stripping column, where it is treated with steam to remove hydrogen sulfide, and any carbon dioxide that may also have dissolved in the alkanolamine. The "lean" alkanolamine is then recycled back to the absorber. The mixture of hydrogen sulfide and carbon dioxide, collectively referred to as acid gases (because they both dissolve in water to form mildly acidic solutions), is passed to a disposal process, such as the Claus process, which is discussed below and later in Chapter 20.

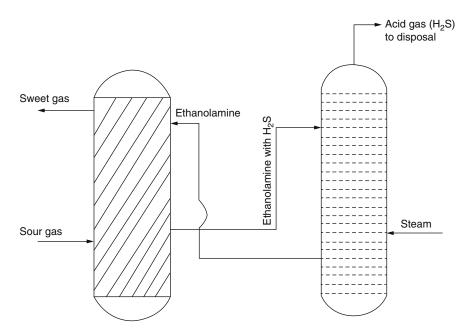


Figure 10.2 A gas sweetening process using ethanolamine as the sweetening agent, followed by steam stripping to liberate the  $H_2S$  and regenerate the ethanolamine.

When the  $H_2S$  content of the gas is very high, there can be value in recovering the sulfur and selling it to, e.g. sulfuric acid manufacturers. The Claus process [H] provides a way of doing this. In a sense, the Claus process can be thought of as mainly a sulfurproduction process, and not a process used specifically for sweetening. The Claus process is often used downstream of other processes that remove hydrogen sulfide from the gas. Recovery of sulfur depends on oxidation of hydrogen sulfide to sulfur, in two steps:

$$\begin{array}{c} H_2S + \frac{1}{2}O_2 \rightarrow H_2O + SO_2\\ 2H_2S + SO_2 \rightarrow 2H_2O + 3S\\ \end{array}$$
  
net : 3 H\_2S +  $\frac{1}{2}O_2 \rightarrow 3H_2O + 3S. \end{array}$ 

The first reaction can be accompanied by direct reaction of H<sub>2</sub>S to sulfur, i.e.

$$H_2S+ {}^1\!\!/_2O_2 \to H_2O+S.$$

Both reactions of hydrogen sulfide with oxygen are thermal processes, occurring above 550°C. The reaction of hydrogen sulfide with sulfur dioxide is a catalytic process at  $\approx$ 370°C. Activated alumina is a useful catalyst.

A process flow diagram is shown in Figure 10.3.

With three catalytic reactors, about 97% of the hydrogen sulfide can be converted to sulfur. Depending on the air quality standards where this plant is operating, the residual sulfur gases (which might include small amounts of carbonyl sulfide and carbon disulfide) and any carbon dioxide present are emitted to the atmosphere. Otherwise, these so-called tail gases from the Claus unit must be treated further to reduce the sulfur emissions even further.

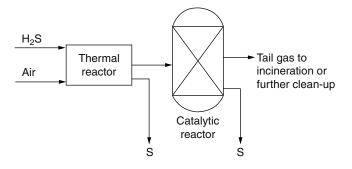


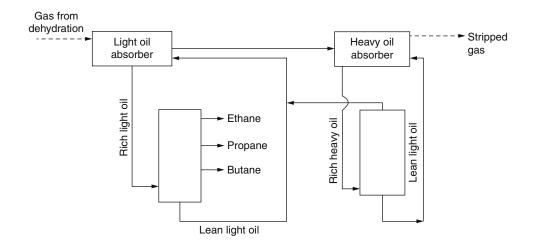
Figure 10.3 The Claus process consists of partial conversion of  $H_2S$  to  $SO_2$  in a thermal reaction, followed by a catalytic reaction of  $SO_2$  with  $H_2S$ .

# 10.1.3 Separation of C<sub>2</sub><sup>+</sup> hydrocarbons

If the gas is also wet, the sweetened gas is passed through a light oil absorber. In this unit, the gas is brought into contact with hexane at  $-20^{\circ}$ C and 3.5 MPa. Since hydrocarbons are neither acidic nor basic, nor capable of hydrogen bonding, strategies used in dehydration and sweetening cannot be used. Instead, the approach is to dissolve the hydrocarbons in a suitable solvent. Based on the rule-of-thumb that "like dissolves like," hexane makes a good solvent for the lighter alkanes. Temperature and pressure conditions are chosen on the basis of the increasing solubility of gases in liquids with decreasing temperature and increasing pressure. The solution of light hydrocarbon gases in hexane is called rich light oil. Fractional distillation of the rich light oil yields ethane, propane, and butane. Unlike the glycols and the ethanolamines, some hexane vapors inevitably appear in the gas. A heavy oil absorber removes the hexane.

Fractional distillation of the condensate from wet gas makes it possible to recover ethane and propane as pure fractions. The distillation must be performed at elevated pressure, to keep some of the components in the liquid phase. The major use of ethane is in the production of ethylene, which in turn is used in enormous amounts ( $\approx$ 110 million tonnes per year) by the petrochemical industry for making such polymers as polyethylene and poly(vinyl chloride) that are nearly ubiquitous in modern life. Ethane heated in the presence of steam to >900°C dehydrogenates to ethylene [I]. At atmospheric pressure propane boils at -42°C, so that it liquefies reasonably easily to, and constitutes the principal component of, LPG.

Natural gasoline can be recovered either by compressing the gas stream until the pressure becomes high enough to liquefy the relatively non-volatile higher alkanes, or by distillation of the liquid from the heavy oil absorber. Natural gasoline can be used as an additive to the gasoline obtained from petroleum distillation, particularly to enhance the vapor pressure of the blend, improving cold-weather starting. Natural gasoline is of relatively low octane number,  $\approx 65$ , not by itself giving good performance in modern high-compression engines. Nonetheless, natural gasoline is used directly as a liquid vehicle fuel in some parts of the world. Nowadays the natural gasoline not used as a blend stock is sold for petrochemical production, primarily for conversion to ethylene. Like natural gas itself, the composition of natural gasoline varies widely from one source to another. In general, the principal components include 30–80% of C<sub>5</sub>



**Figure 10.4** A flow diagram for a process that removes the larger gaseous hydrocarbons from methane.

hydrocarbons, i.e. pentane, isopentane, and 2,3-dimethylbutane; 15–40%  $C_6$  hydrocarbons, hexane, 2- and 3-methylpentane, methylcyclopentane, and cyclohexane; a small amount,  $\approx 1\%$ , of benzene; 5–30%  $C_7$  hydrocarbons such as heptane, the methylhexanes, dimethylcyclopentanes, and methylcyclohexane; a few percent of toluene; and about 5% of the various  $C_8$  hydrocarbons.

Butane and 2-methylpropane (isobutane), referred to as the C<sub>4</sub> cut, are easily liquefied. Butane boils at  $-1^{\circ}$ C. Only a slightly elevated pressure,  $\approx 230$  kPa, is needed to keep it in the liquid phase at ambient temperature. The liquid fuel visible in transparent cigarette lighters is butane. Pentane, 2-methylbutane (isopentane) and 2,2-dimethylpropane (neopentane) comprise the C<sub>5</sub> cut. Depending on the composition and quality of these products, they are used for gasoline blending or for ethylene production.

Figure 10.4 illustrates a sequence of gas processing steps.

After this sequence of operations, the product is sometimes called stripped gas. With addition of small quantities of an odorant, it is finally ready to go into the pipeline for sale to consumers.

Natural gas as eventually supplied to consumers is typically >90% methane, and often close to 100% methane. Methane is both invisible, mixing freely with air, and has no odor. It is also highly flammable, and in  $\approx$ 5–15% mixtures with air, explosive. Some simple way is needed to determine whether natural gas is leaking, to avoid potentially tragic situations [J]. This is done by adding an odorant, so that a natural gas leak can be detected by smell. The odorant is usually a small organic sulfur compound, or mixture of such compounds. A popular component of odorant blends is 2-methyl-2-propanethiol (*tert*-butyl mercaptan), a compound with the rather noticeable aroma of rotten cabbage. While it may seem counterproductive to put sulfur compounds back into a sweetened gas, the small mercaptans and the related sulfides have such horrendous odors that they can be detected easily at the parts-per-million level. The tiny amount of SO<sub>x</sub> produced when the odorant burns is negligible.

Fuel	CO <sub>2</sub> contribution	H <sub>2</sub> O contribution	Total
CH <sub>4</sub>	-393	-570	-963
$C_{10}H_{22}$	-393	-314	-707
$C_{100}H_{80}$	-393	-114	-507

**Table 10.3** Comparison of the contributions of the heats of formation of carbon dioxide and water to the observed calorific values of selected fuels, in kJ per mole of carbon.

# 10.2 Natural gas as a premium fuel

By several criteria, natural gas is *the* premium fuel. On an equal mass basis, combustion of natural gas liberates more energy than any other hydrocarbon fuel [K]. It also produces less carbon dioxide per unit of energy, 0.05 kg  $CO_2/MJ$ . It contains no inorganic, ash-forming components, so leaves no residue on combustion. Sour gas can be sweetened easily, eliminating the problem of sulfur emissions during combustion. Fluids are much easier to handle, meter, and regulate in process or combustion systems than are solids. The low density of gases at ordinary conditions does make it difficult to store a useful weight of gaseous fuel, unless it is compressed to high pressure or stored cryogenically as a liquid. Nevertheless, most natural gas consumers, especially domestic users, can connect directly to the distribution system, eliminating the requirement for on-site storage commonly needed with other fuels.

For pure methane, the enthalpy change for the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

is -892 kJ/mol. In the initial combustion process reaction temperatures are high enough such that the water produced in the reaction is in the gaseous state (i.e. steam). Several factors contribute to natural gas having the highest calorific value among the common fuels. One, the hydrogen content, is discussed here; others recur later in this book. Taking natural gas, as delivered to the consumer, essentially to be pure methane, its H/C ratio is 4. Many petroleum products have H/C of  $\approx 2$ . Decane,  $C_{10}H_{22}$ , can be taken as a representative component of light petroleum products. For humic coals, H/C < 1. We see in Chapter 17 that coals have complex, macromolecular structures, but for now it can be assumed that coal can be represented by the formula  $C_{100}H_{80}$ . If these fuels are burned in oxygen to produce carbon dioxide and liquid water, the enthalpy liberated is that contributed by the formation of these two products, minus the enthalpy of formation of the fuel. The heats of formation of the products are -393 and -285 kJ/mol, respectively. Real petroleum products contain dozens, possibly hundreds, of components, so that the heat of formation can only be represented as a weighted average of the heats of formation of the components, if we know what they are. The heat of formation of coal is a term rarely considered in coal science or technology. To simplify, heats of formation are neglected, and only the contributions of the  $CO_2$  and  $H_2O(l)$  to the overall heating value are considered. And, to make a fair comparison among these fuels, it is helpful to compare on the basis of an equal number of moles of carbon,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
,  
 $CH_{2.2} + 1.55O_2 \rightarrow CO_2 + 1.1H_2O$ ,  
 $CH_{0.8} + 1.2O_2 \rightarrow CO_2 + 0.4H_2O$ .

From this, the contributions of carbon dioxide and liquid water to the enthalpy release can be determined, as summarized in Table 10.3.

Table 10.3 shows that, on the basis of an equal number of moles of carbon, the contribution of the enthalpy of formation of carbon dioxide is the same for each. But the contribution of the enthalpy of formation of water decreases, because the amount of hydrogen in the original fuel has decreased from  $CH_4$  to  $CH_{2.2}$  and again to  $CH_{0.8}$ . This analysis leads to a useful rule of thumb for comparing hydrocarbon fuels: among a group of fuels compared on an equal amount of carbon, the heating value decreases as the H/C ratio decreases. Like most such rules, this one is useful only for a quick, qualitative comparison. The analysis shown in Table 10.3 does not consider heats of formation of the reactants. As discussed in Chapter 17, other factors in addition to H/C ratio influence heating value, particularly oxygen content and aromaticity. But, so long as care is taken to apply the rule only to materials that are reasonably similar, it provides a useful, quick assessment. Within a family of compounds that are closely related chemically, and for which the heats of formation of the reacting molecules are known, the relationship of heat of combustion and H/C ratio becomes quite good. Such a relationship for the *n*-alkanes was shown in Figure 9.13.

## Notes

- [A] People in many countries rely on anaerobic digestion of manure and even of human feces as a source of gaseous fuel. They include probably tens of millions of people in China. The digestors are of simple, "low-tech" design, relatively easy to make. And, the residual solids make good fertilizer.
- [B] As an example, twenty water molecules can associate, via intermolecular hydrogen bonding, to form a pentagonal dodecahedron. The interior of this structure has enough volume to accommodate molecules of methane, as well as other gases such as chlorine molecules or atoms of the noble gases. Frozen methane hydrates can be ignited with a match and will burn, giving rise to informal names such as "the ice that burns." This kind of clathrate formation is not limited to water. For example, aqueous solutions of nickel cyanide can form Ni(CN)<sub>2</sub> clathrates big enough to trap benzene molecules. In similar fashion, the benzene can be ignited and burned.
- [C] Optimists see this as an immense deposit of fuel for future use. Pessimists note that methane is a potent greenhouse gas, a much better infrared absorber than carbon dioxide, and are concerned that if Earth were to warm enough to cause a sudden and massive release of methane from the permafrost, the rapid addition of large quantities of methane to the atmosphere would cause a step change in global warming.

- [D] An interesting exception is a gas deposit near Emory, Texas, USA that contained 42% H<sub>2</sub>S. It must have been a memorable day on the drilling rig when the drill bit punched into that stuff.
- [E] The oxides of sulfur, and of nitrogen, are soluble in water. In the atmosphere, they dissolve in water, and eventually return to the surface in some form of precipitation, e.g. rain, snow, sleet. These solutions can have pH values of 4 to 5, and in very extreme cases  $\approx 1.5$ . This environmental problem is known as acid precipitation, commonly called acid rain. Acid rain has numerous negative effects on the environment, including: acidification of natural waters and the resultant die-off of aquatic life; damage to growing plants including crops and forests; and leaching plant nutrients out of the soil or mobilizing potentially toxic elements. In humans, exposure to acid rain irritates sensitive tissues of the respiratory tract, enhancing susceptibility to disease or exacerbating chronic respiratory problems.
- [F] Radon would be a curiosity meriting a short paragraph in a textbook chapter on the noble gases, if it were not for a potential human health problem. Radon formed from radioactive decay of uranium diffuses through the soil and into buildings via cracks, holes, or joints in the foundations. Because radon itself is mildly radioactive, chronic exposure to radon is thought to lead to cancer. In the United States, the Environmental Protection Agency estimates that twenty thousand lung cancer deaths per year are due to radon exposure, making it the second-leading cause of lung cancer deaths after tobacco.
- [G] Zeolites, first introduced in Chapter 4, comprise an enormous family of aluminosilicate minerals that also contain cations of other elements, and that have particular pore-size dimensions allowing some molecules access to the interior, and excluding others. Even more important than natural gas dehydration is their role in catalytic cracking of petroleum fractions, discussed again in Chapters 13 and 14. The original industrial applications of zeolites relied on naturally available minerals, but nowadays the preference is for synthetic zeolites, because the distribution of pore sizes and the chemical properties of the surface can be optimized for the specific application.
- [H] Invented in the 1880s by the German chemist Carl Friedrich Claus, who was working in England at the time. Few biographical details are available, perhaps because he was overshadowed by his contemporary, the *other* Carl Friedrich Claus, a German zoologist and marine biologist who produced a very influential textbook of zoology.
- [I] As discussed in Chapter 7, larger alkanes can be converted to ethylene via initiation of free-radical processes followed by successive  $\beta$ -bond scission reactions. Ethane is favored, though, because its conversion is highly selective for ethylene production. When larger alkanes are used, intermediate radicals in the propagation steps can undergo reactions other than  $\beta$ -scission, eventually terminating in products other than ethylene.
- [J] In the United States, the practice of adding odorants to natural gas dates to a 1937 tragedy, in which natural gas accumulated, unknown to anyone, in a school building in New London, Texas. It is thought that an electric spark in the motor of a sander used in a workshop class set off the explosion and ensuing fire, which left about 300 students and teachers dead.

[K] The adjective hydrocarbon is important here, because an equal mass of hydrogen will liberate much more energy than methane. The heat of combustion of hydrogen is -142 MJ/kg, compared with -54 MJ/kg for natural gas.

#### **Recommended reading**

- Gayer, R. and Harris, I. *Coalbed Methane and Coal Geology*. The Geological Society: London, 1996. A compilation of research papers, mainly with a European focus, useful for those wanting to learn more about this resource.
- Kohl, A. and Riesenfeld, F. *Gas Purification*. Gulf Publishing: Houston, 1985. A very comprehensive and very useful source of information on natural gas processing and various processes for removing impurities.
- Makogon, Y.F. *Hydrates of Hydrocarbons*. PennWell: Tulsa, OK, 1997. A comprehensive source of information on gas hydrates.
- Melvin, A. *Natural Gas: Basic Science and Technology*. British Gas: London, 1988. A useful treatment of gas technology, such as exploration and measurement of high-pressure flows, not treated here.
- Nelson, W.L. *Petroleum Refinery Engineering*. McGraw-Hill: New York, 1958. Not much information is published nowadays on natural gasoline. This older book is one of the best single sources of material on this resource.

# **11** Composition, classification, and properties of petroleum

Analyzing petroleum samples collected from around the world would show that their elemental compositions vary over only a narrow range: 82-87% carbon, 11-15% hydrogen, with the balance being oxygen, nitrogen, and sulfur. Oxygen and nitrogen seldom exceed 1.5% each, but sulfur can amount to as much as 6% in extreme cases. Yet these samples could show remarkable diversity in physical characteristics, ranging from lightly colored, free-flowing liquid to dark, smelly, highly viscous material. A consequence of the wide variability of physical properties coupled with a very narrow range of composition is that carbon content cannot be used as a simple predictor of properties; in this respect, petroleum is very different from coal (Chapter 17). If these same samples were analyzed to determine the specific chemical compounds present in each, any particular sample would be found to contain some 10<sup>5</sup> individual components, varying in concentration from one sample to another. That is, on an elemental basis, most oils have about the same composition, but on a molecular basis no two are exactly alike. These seemingly disparate properties arise because most components of petroleum belong to a small number of homologous series of compounds, of which the composition, on a weight percent basis, varies only little, even over a long span of the series. For example, pentane,  $C_5H_{12}$ , is 83.3% C and 16.7% H on a weight basis; pentadecane, C<sub>15</sub>H<sub>32</sub>, is 84.9% C and 15.1% H. All possible isomers of all the alkanes between pentane and pentadecane amount to 7666 compounds, yet their elemental compositions change by only 1.6 percentage units. The range of boiling temperatures of the components spans at least 550°C; pentane, the smallest alkane liquid at room temperature, boils at  $36^{\circ}$ C, and some oils contain material that does not boil even at 600 °C.

# 11.1 Composition

Petroleum contains four classes of compound: alkanes, cycloalkanes, aromatics, and heteroatomic compounds with one or more atoms of nitrogen, sulfur, and/or oxygen. In petroleum chemistry and technology, alkanes are called paraffins; cycloalkanes, naphthenes; and the heteroatomic compounds are lumped together as NSOs. Cycloalkanes, aromatics, and NSOs can all have one or more alkyl side chains.

## 11.1.1 Alkanes

Paraffins come primarily from cracking of lipids. *n*-Alkanes of fewer than five carbon atoms are gases at ordinary temperatures and pressures. The largest *n*-alkane liquid at room temperature is heptadecane,  $C_{17}H_{36}$  (melting point 22 °C). Octadecane

(melting point 28 °C) and larger alkanes exist in solution in the petroleum liquid. Supposedly the largest alkane ever found in petroleum is  $C_{78}H_{158}$ .

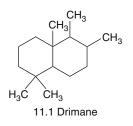
Some oils contain paraffin waxes in their higher boiling point fractions. Wells and pipelines experience trouble when this wax deposits on the walls of the pipes as the oil cools in rising to the surface, or in transmission. Wax also precipitates and clogs pores in reservoir rocks. Some wells produce a substance like the so-called petroleum jellies (or petrolatum) used to formulate ointments and cosmetics, or sold for protecting and softening skin.

Branched-chain alkanes also occur. Some biomarkers have survived nearly unaltered from the original organic matter, such as 2,6,10,14-tetramethylpentadecane (pristane) and 3,5,11,15-tetramethylhexadecane (phytane).

The related alkenes, alkadienes, and alkynes do not occur in petroleum. Alkenes found in many petroleum products result from various processes in the refinery, and not from having been in the oil initially.

#### 11.1.2 Cycloalkanes

Almost all cycloalkanes present in petroleum derive from cyclopentane or cyclohexane. In many cases these structures are remnants of larger cyclic structures present in the original organic matter, e.g. drimane (11.1).

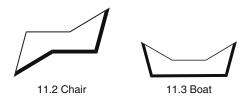


In principle, cyclic molecules could exist with any number of carbon atoms greater than two. Derivatives of the first two cycloalkanes, cyclopropane and cyclobutane, are rare in nature [A]. In cyclopropane, the triangular shape of the molecule forces the C–C–C bond angles to be  $60^{\circ}$ , a very large departure from the preferred bond angle of 109° in the  $sp^3$  orbital configuration of a tetrahedrally hybridized carbon atom. Because of the severe bond strain, cyclopropane and its derivatives readily undergo ring-opening reactions. For example, cyclopropane reacts readily with bromine to form 1,3-dibromocyclopropane. In cyclobutane, the internal angles of a square molecule would be 90°. However, with more than three carbon atoms, all of the atoms need no longer lie on a plane. Not only is the bond strain less for C–C–C bond angles of 90°, but also one of the four carbon atoms can be out of the plane of the other three, increasing the bond angles slightly beyond the 90° of a square. Nevertheless, cyclobutane is still a strained molecule, and also undergoes ring-opening reactions, e.g. easy hydrogenation (at  $\approx 120$  °C) to butane.

A planar, pentagonal molecule would be expected to have internal bond angles of  $108^{\circ}$ , very close to the ideal  $sp^3$  tetrahedral angle of  $109^{\circ}$ . Even if cyclopentane were perfectly planar, which it is not, there would be negligible bond strain. In cyclopentane, one of the five carbon atoms lies slightly out of the plane of the other four. This

configuration, called the envelope configuration by analogy with a common envelope, relieves the bond strain, resulting in cyclopentane being as stable as most non-cyclic alkanes.

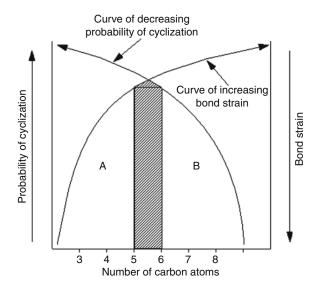
Hexagons have internal angles of 120°. Perfectly planar cyclohexane has significant bond strain resulting from the C–C–C bond angles being forced to spread more widely than the ideal tetrahedral angle. But cyclohexane exists in non-planar configurations that provide bond angles very close to 109° and eliminate strain: the preferred chair, and the boat (11.2 and 11.3, respectively).



(In these structures, three of the carbon-carbon bonds are highlighted for clarity of illustration.)

Heat of formation also provides insights into molecular stability. Among the *n*-alkanes, each  $-CH_{2}$ - methylene group contributes about -20.5 kJ/mol to the heat of formation. That is, the heat of formation of a selected *n*-alkane is greater by about -20.5 kJ/mol than the compound with one fewer carbon atom, and is less by this amount relative to the compound with one more carbon atom. For cyclohexane, the  $\Delta H_f^0$  per methylene group is also -20.5 kJ, suggesting that cyclohexane has the same stability as a typical *n*-alkane. The calculated heat of formation for a perfectly strain-free molecule of cyclohexane would be -123.0 kJ/mol. In contrast, calculated heat of formation for strain-free cyclobutane is -82 kJ/mol, whereas the experimental value is +28.4 kJ/mol, the difference indicating a very high degree of bond strain.

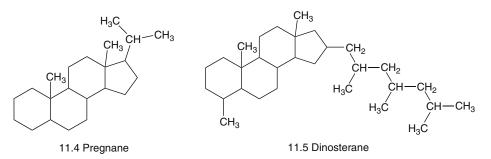
The same strategy for eliminating bond strain, adopting an out-of-plane configuration, serves for cycloalkanes larger than cyclohexane. But cycloheptanes and larger cycloalkanes also rarely occur in nature [B]. Here, a factor other than bond strain comes into play. The cyclic terpene molecules that serve as precursors for cycloalkanes, such as drimane, in petroleum must be products of biosynthesis reactions. And the biosyntheses must involve ring-closure reactions. Ring closures to form cyclopropanes and cyclobutanes are difficult because of the large bond strain in the cyclic products. Cyclopentanes and cyclohexanes have minimal bond strain; compounds based on these structures are widespread in nature. With cycloheptane and larger molecules, a second problem becomes important: the likelihood of achieving ring closure. If a cyclic structure can be considered to be the product of ring closure of a diradical, i.e. •CH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>•, as the values of *n* become larger the likelihood diminishes that one end of the chain will find the other, to complete a radical combination reaction, before another, competing radical process (e.g. hydrogen abstraction or  $\beta$ -bond scission) can occur. For chains longer than about seven carbon atoms, bringing the two ends together to effect ring closure becomes very difficult. Laboratory syntheses of large cycloalkanes must be done in highly dilute solutions, to maximize the chances of bringing the two ends of the molecule together before one of the ends can undergo some other kind of reaction. Figure 11.1 provides a qualitative summary of these



**Figure 11.1** The dominance of five- and six-membered ring cycloalkanes in nature represents a balance between two competing considerations: the high internal bond strain in cycloalkanes of fewer than five carbon atoms, and the decreasing probability of effecting ring closure in cycloalkanes with more than six carbon atoms.

arguments, illustrating that five- and six-membered rings represent the compromise between minimizing bond strain but maximizing the probability of ring closure.

Petroleum also contains a variety of polycyclic naphthenes, of which pregnane (11.4) and dinosterane (11.5) serve as examples.

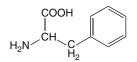


These compounds are also biomarkers. For example, dinosterane derives from the family of aquatic microorganisms, dinoflagellates.

## 11.1.3 Aromatics

In petroleum, the aromatic compounds that are liquids at ordinary temperatures are benzene, toluene, the isomers of xylene, and 1,3,5-trimethylbenzene (mesitylene). Aromatics with condensed ring systems, e.g. naphthalene, phenanthrene, and anthracene, which are solids at room temperature, may be present in solution. Alkylated derivatives of these compounds may also be present. The range of aromatic content in petroleum is from about 10% to over 50%. Unsubstituted aromatic molecules occur mainly in the lighter fractions; in heavier fractions, these molecules commonly have one or more alkyl substituents or connected cycloalkane rings. The content of aromatic compounds has an inverse relationship to API gravity.

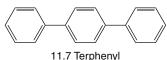
Some aromatics arise from the original organic matter. Some amino acids, e.g. phenylalanine (11.6), contain aromatic structures.



11.6 Phenylalanine

These could be a component of the proteins that contributed to formation of the kerogen. Other aromatics may have formed as a result of aromatization reactions of cycloalkanes, including polycyclic cycloalkanes, during catagenesis.

Polycyclic aromatic hydrocarbons (PAHs), also known as polynuclear aromatic compounds (PNAs), contain two or more aromatic rings fused together. The first compound in the family is naphthalene; other PAHs that could occur in petroleum include anthracene, phenanthrene, and pyrene, as well as their alkylated derivatives. Non-condensed multiring aromatic compounds such as terphenyl (11.7) occur rarely, if at all, in petroleum. The larger polycyclic compounds are divided into two classes based on their solubility in pentane. Soluble components are called resins [C]; those that are insoluble, asphaltenes.



11.7 Terphenyi

Asphaltenes are high molecular weight substances – molecular weights apparently several thousand – the nature and structure of which are still a matter of controversy. They are insoluble in pentane and other lighter alkanes, but dissolve in carbon disulfide, benzene, and chloroform. The elemental composition is approximately 85% carbon, 7-8% hydrogen, <1% sulfur, and 6-7% oxygen, the hydrogen content being a good bit lower than in petroleums in general. The molecular structure may be based on large polycyclic aromatic and naphthenic sheets, with alkyl side chains and incorporation of heteroatoms. Because of their high molecular weight and aromatic character, asphaltenes probably contribute to, or cause, the high viscosity of heavy oils. Some of the solid bitumens discussed later in this chapter contain high proportions of asphaltenes.

Hydroaromatic compounds relate to the PAHs, but in this family at least one of the rings is fully saturated. That is, these multi-ring compounds contain at least one aromatic ring and at least one naphthenic ring. The archetype of the hydroaromatic compounds is tetralin (11.8).



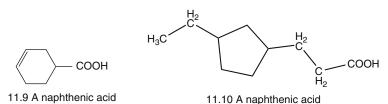
11.8 Tetralin

Multi-ring compounds in the heavier fractions of petroleum tend to be hydroaromatics and their alkylated derivatives.

#### 11.1.4 Heteroatomic compounds

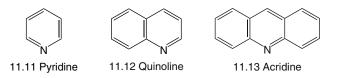
In principle, the so-called NSOs could contain any of the functional groups of nitrogen, sulfur, and oxygen. Nitrogen and sulfur are undesirable. Oxides of both elements, if allowed to escape into the environment after combustion, contribute to the formation of acid rain. Nitrogen oxides also interact with carbon monoxide and unburned fuel molecules, in the presence of sunlight, to produce the air pollution problem known as smog [D, E]. These concerns have led to significant efforts to reduce, or remove entirely, the nitrogen and sulfur in fuels. Oxygen compounds have lower heats of combustion than their purely hydrocarbon analogs. This affects particularly the biofuels, and can also be shown (Chapter 17) to have an effect on the heats of combustion of various coals.

Oxygen occurs in petroleum as phenols, carboxylic acids, and possibly alcohols, esters, and ketones. The carboxylic acids include fatty acids, shorter-chain alkyl carboxylic acids, and naphthenic acids. Naphthenic acids, a family of numerous compounds from simple single-ring acids to complex structures with molecular weights approaching 1000 Da, appear to be one of the most prevalent forms of oxygen compound. Two smaller naphthenic acids are shown as examples in structures 11.9 and 11.10.

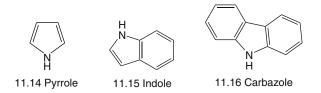


Naphthenic acids cause concern for refining, because they can corrode pipes, valves, and metal processing equipment.

Most crude oils contain less than 1% of nitrogen compounds. Basic nitrogen compounds primarily consist of pyridine (11.11) and its homologs, such as quinoline (11.12) and acridine (11.13).



Their alkylated derivatives may also be present. The non-basic nitrogen compounds are pyrrole (11.14), indole (11.15), and carbazole (11.16), and their derivatives.



As a rule, the more asphaltic the oil (discussed below), the higher its nitrogen content.

Oils that contain dissolved hydrogen sulfide are called sour crudes. Strictly speaking, if an oil contains sulfur in some other form than  $H_2S$  (which often is the case), it should be called a high-sulfur crude and not a sour crude. However, oils containing appreciable sulfur in any form are often referred to loosely as sour crudes. Hydrogen sulfide is

common in many crude oils; if these oils are accompanied by gas, the gas is usually sour as well. Very low-sulfur crudes (0.1–0.2% sulfur) come from Africa, particularly Algeria, Angola, and Nigeria. Pennsylvania crude oils with high API gravities tend to be very low sulfur as well. An intermediate sulfur content would be considered to be in the range 0.6–1.7%; high-sulfur, more than 1.7%. At the other extreme, heavy crudes could contain  $\approx$ 5% sulfur, e.g., some of the oils from Mexico. Generally, sulfur content has an inverse relationship to API gravity.

Sulfur compounds include alkanethiols (mercaptans), thioalkanes and thiocycloalkanes (sulfides), dithioalkanes (disulfides), thiophenols, and heterocyclic compounds derived from thiophene. Younger oils may contain small amounts of elemental sulfur. Its presence is undesirable because, when the oil is processed at temperatures >100 °C, sulfur reacts with hydrocarbons to produce hydrogen sulfide. The reaction of sulfur with cyclohexane provides an example:

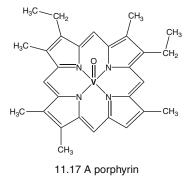
$$+3S \longrightarrow +3H_2S$$

The negative characteristics of sulfur-containing compounds arise from their ability to corrode metal parts in pipelines, refineries, or fuel handling systems; and from their formation of SOx on combustion, which must be captured and dealt with for environmental protection. And, they stink. Butanethiol is one of the compounds responsible for the reek of a freshly flattened skunk.

## 11.1.5 Inorganic components

Petroleum often contains small amounts of two types of inorganic compounds. Ionic compounds derive from contact of the oil with brines in the reservoir. The predominant example is sodium chloride. When the amount of sodium chloride exceeds  $\approx 0.06$  g/l, the oil must be "desalted" before refining (Chapter 12) because of the potential corrosive effects of chlorides on metal refinery piping and vessels.

Coordination compounds, specifically metal porphyrins, make up the other type. These porphyrin compounds usually contain nickel or vanadium as the central metal (e.g. 11.17).



Most oils contain small amounts – i.e. at the parts per million level – of compounds containing vanadyl and nickel porphyrins. Nickel occurs in the range 20 to 85 ppm, largely in low-sulfur oils. Generally, lighter oils contain smaller amounts of vanadium and nickel than heavy oils. In part, this is due to asphaltenes being major contributors to the metal content of heavy oils. The Boscan crude oils of the Lake Maracaibo region of Venezuela contain about 1100 ppm vanadium, offering the potential that these oils could be exploited as vanadium ores, and indeed the world's vanadium needs could probably be met from this single source.

# 11.2 Classification and properties of petroleums

## 11.2.1 API gravity

Oils with API gravities greater than  $40^{\circ}$  are said to be light oils. Heavy oils are usually taken as those that have gravities less than  $20^{\circ}$ , with "heavier" or "extra heavy" oils having  $10-15^{\circ}$  gravities, and bitumens (discussed below) about  $5-10^{\circ}$ . Intermediate oils would be in the  $20-40^{\circ}$  range. The relationships of API gravity with the content of aromatic compounds and sulfur-containing compounds were discussed in Chapter 9. In a light oil, the content of true hydrocarbon compounds (i.e. not NSOs) could be  $\approx 97\%$ , while it might be less than 50% in heavy crudes. Heavy oils were likely to be formed at the top of the oil window. In addition to having high density, they tend also to have high viscosity, high boiling temperature, and possibly high concentration of sulfur. Light oils on the other hand have low density, low viscosity, and usually low sulfur. They are likely to have formed near the bottom of the oil window.

#### **11.2.2** Carbon preference index

The carbon preference index (CPI) indicates the predominance of odd-number carbon chains among the alkanes in a sample of petroleum. The CPI is calculated from

$$CPI = (1/2)[(\Sigma O / \Sigma E_1) + (\Sigma O / \Sigma E_2)]$$

where  $\Sigma$  O is the sum of alkanes with an odd number of carbon atoms in the range from C<sub>17</sub> to C<sub>31</sub>,  $\Sigma$  E<sub>1</sub>, the sum of alkanes with an even number of carbon atoms in the range C<sub>16</sub> to C<sub>30</sub>, and  $\Sigma$  E<sub>2</sub> is defined similarly, except that the range of alkanes is C<sub>18</sub> to C<sub>32</sub>.

Naturally occurring fatty acids have an even number of carbon atoms in the chain (Chapter 5). When a fatty acid experiences thermally induced decarboxylation during catagenesis, the loss of one carbon atom from the chain necessarily results in alkanes having odd numbers of carbon atoms, e.g.

$$CH_3(CH_2)_{15}CH_2COOH \rightarrow CH_3(CH_2)_{15}CH_3 + CO_2.$$

Catagenesis of large alkanes proceeds by C–C bond cleavage, which can occur almost at random along the chain. Beginning with an alkane having an odd number of carbon atoms, one of the fragments necessarily has an even number [F]. Whether these radicals terminate with hydrogen abstraction, or propagate into other radical reactions, the proportion of carbon chains with an even number of carbon atoms gradually increases. A geologically young oil will have experienced little catagenesis, so is likely to contain

a high proportion of alkanes with odd numbers of carbon atoms. Its CPI will be high. Alkanes from recently deposited sediments may have CPI values of 4 to 5. As catagenesis progresses, and the alkane chain lengths become "scrambled" with a steady increase in compounds with an even number of carbon atoms, the CPI decreases. Alkanes from geologically ancient bitumens have CPI values  $\approx 1$ . Alkanes can be determined quantitatively and easily by gas chromatography, so that calculation of the CPI and estimating the age of the oil are straightforward.

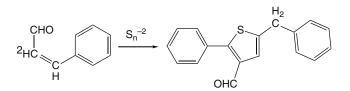
#### 11.2.3 Age–depth relationships

The extent of catagenesis is determined largely by reaction temperature and time for which the reaction is carried out. For petroleum, the time at temperature is determined by its geological age. The temperature itself is determined by the depth of burial, because of natural geothermal gradients. Knowing the value of the geothermal gradient in a specific area allows using depth as an indicator of temperature. Therefore the time-temperature relationship important in laboratory or industrial operations becomes an age-depth relationship for expressing the geological classifications of oils. For convenience, two qualitative values can be taken for age, young or old; and for depth, shallow or deep. Doing so gives four qualitative categories used to classify age-depth relationships: young-shallow, young-deep, old-shallow, and old-deep.

A young-shallow oil has seen relatively low temperatures for a geologically short time. Alkanes in this oil are likely to be large, having experienced little catagenesis. Based on structure-property relationships (Chapter 9), this oil can be expected to be viscous, of low API gravity, and in a high boiling range. Hydrogen redistribution inevitably accompanying catagenesis leads to formation of aromatics, which, at this stage, are likely to be soluble in the oil. At the top of the oil window some biochemical reactions could still be occurring, such as anaerobic conversion of sulfate to hydrogen sulfide, e.g.

$$C_6H_{12}O_6 + 3SO_4^{-2} \rightarrow 3H_2S + 6HCO_3^{-1}$$
.

Hydrogen sulfide dissolved in the oil makes it sour. The sulfur from hydrogen sulfide can be incorporated into organic compounds, via conversion of  $H_2S$  to hydrogen polysulfides,  $H_2S_n$ . Polysulfides react with a variety of compounds formed during diagenesis, e.g. with cinnamaldehyde:



Such reactions result in a high-sulfur oil.

Young–shallow crudes are not desirable refinery feedstocks. They are difficult to pump, have low yields of distillate products in the initial distillation (Chapter 12), and require treatment to remove or reduce the amounts of sulfur and of aromatic compounds. Lots of effort will be required to convert this oil into clean, marketable fuel products.

At higher temperatures, catagenesis proceeds to a greater extent, and, with greater cracking, molecular sizes are smaller. As a result, young-deep oil is of lower boiling range and lower viscosity than young-shallow oils. Young-deep oils form in the middle to bottom of the oil window. Because C–S bonds are weaker than C–C bonds (about 270 vs. 350 kJ/mol, respectively), as catagenesis proceeds the sulfur content of the oil decreases. Further catagenesis also increases the need for hydrogen in the hydrogen redistribution processes. Hydrogen redistribution occurs with formation of increasingly large aromatic molecules, which, as their size grows, are less and less soluble in a liquid phase that is mainly a mixture of alkanes and cycloalkanes. These large aromatic molecules precipitate from the oil as a separate phase, the asphaltenes. Overall, the boiling range, viscosity, aromatic content, and sulfur content of these oils are all lower than for a young-shallow oil.

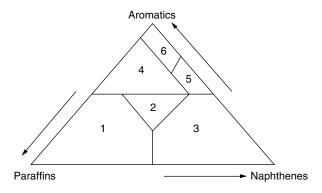
Many geological processes have an approximate interchangeability of time and temperature. A long time at low temperature can eventually produce the same result as a shorter time at higher temperature [G]. Because of that, old–shallow oils can be expected to have many of the same characteristics as young–deep oil. The reduced solubility of gases in liquids as temperature increases means that  $H_2S$  is less soluble in deep oil relative to shallow oil. An old–shallow oil is more likely to be sour than an otherwise similar young–deep oil.

Old–deep oil has experienced the highest temperatures for long times, at the bottom of the oil window. This oil will have cracked about as far as possible without being converted completely to gas. With small molecules, the oil tends to be rich in relatively low-boiling distillate products and be of low viscosity. Hydrogen redistribution will have proceeded extensively, with a loss from the oil of large aromatic molecules. Organosulfur compounds will have converted to  $H_2S$ , which is of low solubility in the liquid at high temperature. Old–deep oils are sweet, low-sulfur, low-viscosity oils usually providing good yields of distillate products. The aromatic content is also low. Old–deep oils are the antithesis of the young–shallow oils, and are highly desirable refinery feedstocks.

Oils of the old-deep category were found first in Pennsylvania, which was the original home of the oil industry in the United States. The standard of high-quality oil, regardless of where it actually comes from, is still called Pennsylvania crude, or sometimes Penn-grade crude. A good Pennsylvania crude has an API gravity of  $45-50^{\circ}$ , sulfur content of <0.1%, low aromatics, and low viscosity. Much of the world's Penn-grade crude has already been used, so that nowadays less than 2% of the world's oil is of this quality. Refiners must deal with oils of poorer quality, or, as it has been said: "The world is becoming increasingly sour" [H]. Refiners must work harder and harder to produce the enormous amounts of clean liquid fuel products demanded by the marketplace.

## 11.2.4 Composition relationships

The age-depth system classifies petroleum based on a geological perspective. An alternative approach classifies oils based on their chemical composition. This second approach, which may be more useful for fuel chemistry or fuel process engineering, represents a greater focus on the eventual end use of the oil, rather than on its origins.



**Figure 11.2** A ternary classification diagram for crude oils. The regions represented in this figure are (1) paraffinic, (2) paraffinic-naphthenic, (3) naphthenic, (4) aromatic-intermediate, (5) aromatic-naphthenic, and (6) aromatic-asphaltic.

Classification of petroleum in terms of composition is based on the amounts of alkanes (paraffins), cycloalkanes (naphthenes), and aromatics in the oil. The *aromatic* NSOs are lumped with the aromatic hydrocarbon compounds. The system is based on the ternary diagram shown in Figure 11.2.

Several classification systems exist, based on the proportions of the various classes of compound in the oil. One such recognizes six types:

- (1) Paraffinic crudes generally contain <1% sulfur; have API gravities above 35°, and have total paraffins and naphthenes >50%, with paraffins >40%.
- (2) Paraffinic-naphthenic crudes usually also contain <1% sulfur, and also have total paraffins and naphthenes >50%, but neither paraffins nor naphthenes can be >40%.
- (3) Aromatic-intermediate crudes generally contain more than 1% sulfur, have aromatic contents >50% and paraffins >10%.
- (4) Aromatic-naphthenic crudes usually contain <1% sulfur but >25% naphthenes, with aromatic content >50% and paraffins <10%.
- (5) Aromatic-asphaltic oils have >1% sulfur but <25% naphthenes, >50% aromatics, and <10% paraffins.</p>
- (6) Asphaltic crudes fall outside the definition of type 5. Types 4, 5 and 6 are usually heavy crudes that may have formed by degradation of lighter oils. The Athabasca tar sands (discussed below) fall into type 5.

About 85% of the world's oil falls into the paraffinic, intermediate, or naphthenebase types. Paraffin-base crudes now contribute only a tiny fraction of the total world oil supplies, because they have been so heavily utilized in the past. The great majority of remaining oil is paraffinic-naphthenic. This type includes nearly all the oil in Middle East, in mid-continental United States, and in the North Sea.

Oils are also classified simply according to the dominance of a particular type of hydrocarbon, as paraffinic-base, naphthenic-base, or mixed-base (naphthenicparaffinic) oils. Aromatics rarely dominate. If the distillation residue consists largely of asphalts, the crude is said to be asphaltic, or asphalt-base oil. Asphalt-base crudes are dominated by the naphthenes, which include not only simple naphthenes such as cyclohexane and decalin derivatives, but also much more complex asphaltic

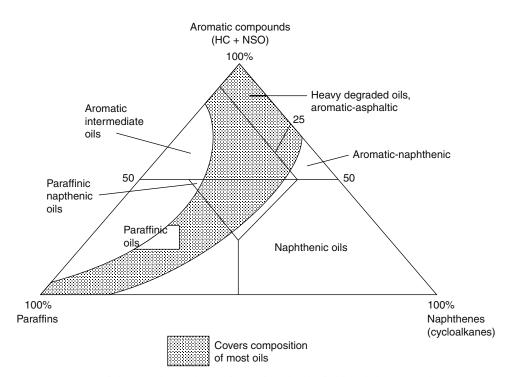


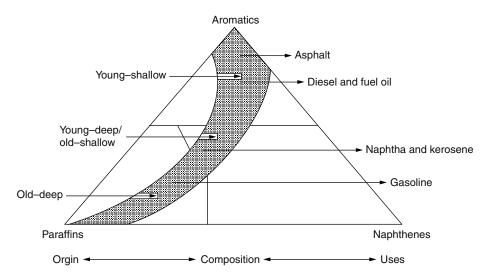
Figure 11.3 Most of the world's crude oils fall within the shaded band shown on this ternary diagram.

molecules that contain large polycyclic ring systems made up of both naphthenic and aromatic rings. The so-called black oils from Mexico, Venezuela, and Russia, as well as oils from California and the Gulf coast of the United States, fall into this category.

Since the axes of the ternary diagram of Figure 11.2 each scale from 0 to 100%, the diagram implies that oils can exist with literally any possible composition. In reality this does not happen. The vast majority of the world's oils have compositions that lie somewhere in the relatively narrow band shown in Figure 11.3.

As catagenesis proceeds, increased cracking results in smaller molecules in the oil, which have lower boiling temperatures. When an oil is distilled, the extent to which a given distillation fraction (such as gasoline, kerosene, or diesel fuel) dominates among the products depends on the composition of the oil. Composition depends, in turn, on the extent of catagenesis. Consequently, age and depth help to determine the range of molecular size in the oil, which establishes distillation behavior, and which in turn helps indicate which products will be the major fractions from distillation [I]. These approximate relationships are illustrated in Figure 11.4. This figure illustrates the major foundations of the discipline of fuel science: how the origin of the fuel determines its composition and properties, and how the composition and properties then affect its behavior when it is used.

The Watson characterization factor, also known as the UOP (for Universal Oil Products Company) factor, was developed initially as a means of predicting or correlating the behavior of oils in thermal cracking processes (Chapter 16). It is given by the equation



**Figure 11.4** This diagram relates the classification of oils in the age–depth system with their likely positions on the ternary composition diagram and the dominant product obtained from simple processing of the oil.

$$K_{\rm W} = (T_{\rm b})^{1/3} / {\rm sp.gr.},$$

where  $T_{\rm b}$  is the average boiling point in degrees Rankine and sp.gr. is the specific gravity at 15 °C (60 °F). A modified version, using temperature in kelvin, is

$$K_{\rm W} = (1.8 T_{\rm b})^{1/3} / {\rm sp.gr.}$$

For pure compounds, the value of the normal boiling point in appropriate units is used.  $K_W$  can be as high as 15 for some alkanes, and less than 10 for aromatic compounds. Since plenty of physical property data are known for pure compounds,  $K_W$  is more useful in determining the character of crude oils or of distillation cuts. For those cases, an average boiling point must be used. For crude oils, the average is calculated from

$$T_{\rm b} = (T_{20} + T_{50} + T_{80})/3,$$

while for distillation fractions

$$T_{\rm b} = (T_{10} + 2T_{50} + T_{90})/4,$$

where in both equations  $T_n$  is the temperature at which *n* percent by volume has distilled. Typically,  $K_W$  is 11–13 for paraffinic feeds, 10–11 for naphthenic feeds, and <10 for aromatics.

The correlation index (CI), developed by the U.S. Bureau of Mines, is found from

$$CI = 473.7 \text{ sp.gr.} - 456.8 + (48640/K)$$

where K is the average boiling point in kelvin and sp.gr. is the specific gravity. Values between 0 and 15 indicate a predominance of paraffinic hydrocarbons, from 15 to 50, a predominance of either naphthenes or mixtures of paraffins, naphthenes, and aromatics, and above 50, a predominance of aromatics.

The quality of a given sample of oil is specified by its crude assay, which reports the values of acid number, API gravity, characterization factor, distillation curve, pour point, sulfur content, and viscosity. Acidity is measured by titration with potassium hydroxide solution. The results are expressed as the acid number, the milligrams of potassium hydroxide required to neutralize one gram of the oil. The pour point is the temperature at which the oil ceases to flow; it provides an approximate guide to how easy it would be to pump the oil, especially under low-temperature conditions. Measurement of the pour point consists of cooling a sample of oil until it no longer flows when the sample container is held horizontally for five seconds. Oils with high concentrations of large alkanes that crystallize or precipitate as waxes tend to have high pour points.

## 11.3 Asphalts, oil sands, and other unconventional oils

Many places around the world have deposits of viscous, plastic hydrocarbons that appear to be solid at ambient temperature because their viscosity is so high. These materials are known by various colloquial, sometimes colorful, names. Several concepts have been developed to explain their origin.

These naturally occurring solid or semi-solid hydrocarbons can be divided into several categories. Native bitumens consist of high-molecular-weight alkanes, usually  $C_{22}^+$ , and some NSOs. Reservoir bitumens are formed by *in situ* alteration of petroleum already collected in a reservoir. The alteration may be due either to a continuation of catagenesis, or to "deasphalting." Asphaltenes are insoluble in light hydrocarbons; if natural gas is present in the reservoir, some will dissolve in the oil, and help to precipitate asphaltenes. This type of reservoir bitumen often consists mostly of true hydrocarbons, with only very small amounts of NSOs. They also contain a greater amount of aromatic carbon, incorporated in larger condensed-ring systems, than do most of the native bitumens. These materials lie along the carbon-rich pathway of the "inverted-V" hydrogen transfer diagram. They are relatively insoluble in most common organic solvents. Another category of reservoir bitumens is formed at or near the surface under low-temperature conditions through degradation of oil by inspissation (described below), water washing, and possibly attack by microorganisms. This type of reservoir bitumen is generally soluble in organic solvents, and physically seems to be plastic or tar-like.

Inspissation begins when a pool of petroleum migrates to the Earth's surface. Several processes then seem to come into play. Small hydrocarbon molecules having appreciable vapor pressure at ambient temperatures can evaporate. Exposure to meteoric water [J] also results in slow removal of small hydrocarbons. The water solubility of hydrocarbons, not high to begin with, decreases with increasing molecular size, as indicated in a comparison of pentane, at 0.036 g/100 ml, with octane, 0.0015 g/100 ml. Oxidation by exposure to air can significantly increase solubility, as exemplified by data for a family of  $C_5$  compounds in Table 11.1.

As reaction with atmospheric oxygen proceeds, the solubility of small, oxidized molecules in water increases greatly. With larger hydrocarbons, the effect illustrated for the  $C_5$  compounds is still evident, but not nearly so pronounced. 1,8-Octanedioic acid (suberic acid) has a water solubility of 0.14 g/100 ml, a significant increase relative to the parent octane, but much smaller than the solubility of 1,5-pentanedioic

Compound	Formula	Solubility in water, g/100 ml
Pentane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.036
1-Pentanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	2.7
Pentanoic acid	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	3.7
1,5-Pentanedioic (glutaric) acid	HOOCCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	64

**Table 11.1** The effect of increasing oxygen content on the water solubility of C<sub>5</sub> compounds.

acid. Oxidized species from the larger hydrocarbons are more likely to remain in the deposit. Inspissation results in a material containing large molecules, some of which may be partially oxidized, and with very low volatility, low API gravity, and high viscosity. The elemental composition of inspissation products is similar to that of petroleum, slightly lower in carbon and hydrogen and slightly higher in heteroatoms.

Inspissated deposits consist of heavy hydrocarbons, indicating that any light fraction originally present has been removed. Where an accumulation of oil has come to the surface, contact with meteoric water dissolves products of oxidation or biochemical degradation. If the oil had been under pressure in the subsurface, lighter hydrocarbons may come out of solution as vapor when the pressure drops. Or, as oils are exposed to the surface, the lighter liquid components may simply evaporate. The net effect is that the oil is proportionately enriched in viscous, heavy hydrocarbons.

An alternative process leading to formation of heavy hydrocarbons presumes that they have never experienced extensive catagenesis. Several observations support this notion. First, some asphaltic materials contain porphyrins that clearly derived from the organisms that contributed to the original organic matter. That such compounds persist suggests that the sediment never experienced severe reaction conditions. Second, as a rule the amount of free liquid hydrocarbons increases with increasing depth within the Earth, down to the bottom of the oil window. In contrast, the amount of asphaltic and similar materials is inversely proportional to depth. Some heavy hydrocarbons might simply be "very young–very shallow" oils.

Several lines of evidence suggest that most of these natural solid or semi-solid materials form from degradation of conventional oil, and are not very young-very shallow oils. Gases collected from oil sands in Alberta contain acetaldehyde. Acetaldehyde comes from decomposition of pyruvic acid, which itself arises from the actions of anaerobic bacteria (Chapter 4). Since the aldehyde functional group is fairly reactive, the acetaldehyde is likely to have formed recently, indicating that microbial action might be continuing. In the La Brea tar pit, in downtown Los Angeles, the occasional formation of gas bubbles also indicates some continuing chemical or biochemical activity. For this deposit specifically, the surface level has been slowly rising since an earthquake in 1971, suggesting that possibly oil is seeping upward from some subsurface accumulation.

By far the most important commercial material is the viscous, dense (API gravities of  $5-15^{\circ}$ ) hydrocarbons associated with highly porous sands. These materials have often been referred to as tar sands or bituminous sands, but nowadays the preferred name is oil sands. The oil is too heavy and viscous to be extracted by conventional drilling, as would be used for extraction of petroleum. Viscosities are typically >10000 mPa·s.

So long as the recoverable hydrocarbon material is at least 0.08 l/kg, and preferably at least double that, the oil sand has the potential of commercial exploitation.

The sulfur content of the oil can be as low as 0.5%, ranging upward to 6–8% for oil sands in Trinidad. Deposits in Mexico, called chapoptes, represent the extreme case, with about 11% sulfur. Some of the sulfur compounds include benzothiophene and dibenzothiophene, which are not easy to remove in subsequent refining operations (Chapter 15). Most oils recovered from oil sands tend to be rich in ashpaltenes and resins, but with lower concentrations of alkanes compared with conventional oils.

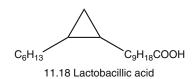
From the perspective of the United States and of Canada, the Athabasca oil sand deposits are of steadily increasing importance. Canada is now the leading source for oil imports into the U.S. Most, if not all, of the refineries in the northern tier of the United States are likely to obtain some oil from these oil sands. The oil is asphaltic, with an API gravity of about 10.5°. The sulfur content is about 5.5%. The oil contains 350–550 ppm vanadium porphyrins.

Oil shales represent an immense resource of hydrocarbons worldwide, probably second only to coal. A distinction between oil shales and oil sands is that in the latter, the oil is free, occurring within interstitial spaces between grains of sand, whereas in oil shales the oil is still locked up in kerogen. Most oil shales are non-marine limestones or marls (i.e. clay mixed with calcium carbonate or calcium magnesium carbonate) containing organic matter. Some silicate minerals might also be included. Most of the kerogen is Type I (algal). The organic content might be in the range 10 to 50%. The lower limit of 10% is the amount usually taken, somewhat arbitrarily, for shale to be considered to be an "oil" shale. The organic material in oil shale contains three fractions: most is kerogen; a much smaller fraction is bitumen, soluble in various organic solvents; and a tiny fraction is an insoluble material that is inert during pyrolysis.

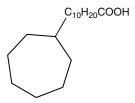
Producing oil from oil shales requires pyrolysis, to force the catagenesis of kerogen in the shales. This can be done above ground in kilns, or underground with the shale still in place. Oil from sapropelic shales is highly paraffinic but also high in sulfur. If the shale has a large input of humic material, the oil tends to be less paraffinic. Components of the oil include alkanes and cycloalkanes from about  $C_{12}$  to  $C_{33}$  and aromatics, carboxylic and amino acids, and porphyrins. The oil generally is heavier than conventional oils, more viscous, and often waxy. Additionally there are more alkenes than in conventional oils. Of greatest concern is the much higher content of NSOs, which indicate that substantial downstream refining will be needed to produce marketable products.

## Notes

 [A] Actually, numerous natural products contain small rings. One example is lactobacillic acid (11.18).



[B] Numerous natural products contain rings larger than cyclohexane. An example is 11-cycloheptylundecanoic acid, a cycloheptyl fatty acid (11.19)



11.9 11-Cycloheptylundecanoic acid

- [C] In this context, the term resin is an operational definition, based on whether a material is, or is not, soluble in pentane, and otherwise conveys no information about molecular structure. These resins are not the same as the plant constituents discussed in Chapter 6.
- [D] Strictly speaking, this phenomenon is known as photochemical smog, to differentiate it from a different form of air pollution, sulfuric acid smog. The latter problem arises when  $SO_3$  is adsorbed onto particulate matter, such as soot or fly ash.  $SO_3$  is extremely hygroscopic, attracting water to form fine droplets of sulfuric acid surrounding the soot or ash particles. A suspension of these droplets in air forms a sulfuric acid smog, an extremely nasty form of air pollution. Fortunately, improvements in desulfurization of fuels and in post-combustion capture of sulfur oxides and particulate matter have largely eliminated sulfuric acid smog as an airpollution problem in most industrialized nations. Nowadays when the term *smog* is used, it is generally understood to refer to photochemical smog.
- [E] Nitrogen oxide also arises from the reaction of nitrogen in the air used in the combustion system with oxygen at the high temperatures of the combustion process, e.g.  $N_2 + O_2 \rightarrow 2$  NO. Because of this, it is possible for a fuel that contains no nitrogen whatsoever still to produce nitrogen oxide emissions during combustion. To differentiate between these two sources of nitrogen oxides, the terms fuel NOx and thermal NOx are used.
- [F] This is a consequence of the inexorable nature of mathematics. Consider undecane,  $C_{11}H_{24}$ , as a simple example. C–C bond cleavage in this compound can produce five pairs of fragments:  $C_1 + C_{10}$ ,  $C_2 + C_9$ ,  $C_3 + C_8$ ,  $C_4 + C_7$ , and  $C_5 + C_6$ . Every pair has one even-number chain. An odd number is always the sum of an even and an odd number; even numbers can be the sum of two even numbers or of two odd numbers.
- [G] This relationship is not confined to geology, and sometimes can be exploited in the laboratory, processing plant, or even at home in the kitchen. It is the basis of the urban legend that it is possible to roast thoroughly a Thanksgiving turkey in a half-hour by setting one's oven on the "self-clean" cycle, which creates temperatures of about 500 °C.
- [H] I owe this comment to John A. Dutton, former Dean of the College of Earth and Mineral Sciences at The Pennsylvania State University.
- [I] As discussed in Chapters 14–16, the major products of distillation are not necessarily the major products of the refinery. Much effort goes on inside the refinery to convert the fractions initially obtained during distillation into the products that eventually come out of the refinery gate to us, the consumers.

[J] Meteoric water is a general term for groundwater that originated in the atmosphere (obviously rain is a major, but not the only, contributor) and percolates or infiltrates through the soil.

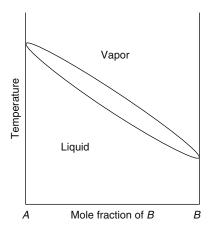
#### Recommended reading

- Berkowitz, Norbert. *Fossil Hydrocarbons*. Academic Press: San Diego, 1997. This book contains useful information on oil shales, heavy oils, and bitumens.
- Bordenave, M.L. *Applied Petroleum Geochemistry*. Editions Technip: Paris, 1993. Several chapters apply, particularly I.6, II.4, and III.1.
- Lee, S., Speight, J.G., and Loyalka, S.K. *Handbook of Alternative Fuel Technologies*. CRC Press: Boca Raton, FL, 2007. Chapters 7 and 8 discuss the production of liquids from oil sands and from oil shales.
- Levorsen, A.I. *Geology of Petroleum*. W.H. Freeman: San Francisco, 1954. Though now very old, and dated in some parts, this book is a classic in its field, and still very useful. Chapter 8 has useful background material for this present chapter.
- North, F.K. *Petroleum Geology*. Allen and Unwin: Boston, 1985. A solid text in this field. Chapters 5 and 10 contain information relevant to this chapter.
- Orr, W.L. and White, C.M. *Geochemistry of Sulfur in Fossil Fuels*. American Chemical Society: Washington, 1990. An edited compilation of research papers; many of the chapters in this book relate to organosulfur compounds in petroleum, and how they got there.
- Selley, R.C. *Elements of Petroleum Geology*. W.H. Freeman: New York, 1985. A useful book, probably proportionately heavier on geology and less so on chemistry, but very good background material. Chapters 2 and 9 relate to the present chapter.
- Sheu, Eric Y. and Mullins, Oliver. *Asphaltenes*. Plenum Press: New York, 1995. The first four chapters of this book provide detailed information on structures and properties of asphaltenes, though this topic remains controversial and other interpretations have been vigor-ously expressed by other scientists.
- Speight, J.G. *The Chemistry and Technology of Petroleum*. Marcel Dekker: New York, 1991. A comprehensive monograph in this field, and a trove of useful information. Chapters 6 and 7 are especially relevant to the material in this chapter.

Petroleum goes through multiple operations intended to separate it into fractions, to improve product quality (e.g. by removing sulfur), and to enhance yields of the more valuable fractions relative to those for which there is less demand. Collectively these operations comprise the technology of oil refining. The objective of refining is to convert petroleum into useful, marketable products through processes that are both economically feasible and environmentally acceptable. Considering on the one hand the complexity and variability of petroleum, and on the other hand the demands imposed for meeting economic and environmental criteria, it is remarkable that petroleum products cost us, the consumers, as little as they do. The primary products of refining are liquid fuels mainly used in the transportation sector, and to a lesser extent for space heat, process heat, or raising steam for electricity generation. Secondary products include feedstocks for the chemical and polymer industries, and carbon materials. The refining situation faces a third constraint, in that the quality of the crude oil available to refineries is slowly but steadily decreasing. Over a century, the API gravity of crudes processed in refineries has dropped from  $30-40^{\circ}$ , typical of oils processed in the late nineteenth century, to  $15-30^{\circ}$  by the end of the twentieth century.

Generally, the desirable and valuable products that can be made from petroleum have H/C ratios higher than those of the petroleum itself. Two strategies provide routes to these products. One is to increase the hydrogen content by adding hydrogen from an external source. Examples include hydrogenation (e.g. conversion of aromatics to cycloalkanes) and hydrocracking, discussed in Chapter 15. The alternative involves removing carbon, known as carbon rejection. The folk saying "If you can't raise the bridge, lower the river" relates directly; the numerical value of any ratio can be increased by increasing the numerator or reducing the denominator. Many thermal processes discussed in Chapter 16 yield, in addition to the desired light products, highly aromatic tars or solid carbonaceous residues as the rejected carbon.

Petroleum has virtually no applications in which it is used directly as it comes from the ground [A]. Near the well site, it can be used "as-is" in furnaces or diesel engines adapted to the characteristics of that particular oil. But the most efficient use of fuel throughout the energy sector requires both a narrow range of properties and consistent properties, so that engines or stationary equipment can be designed for optimum utilization of a specific fuel. Petroleum consists of tens of thousands of compounds. The narrowest range of properties, and the utmost in consistency, can be achieved by using pure compounds as fuels. In principle, though probably with great difficulty in practice, each of the components of petroleum could be separated and recovered, one by one. Since most are present in very low concentration, <1%, and since many have similar chemical and physical properties, the separation processes are likely to be



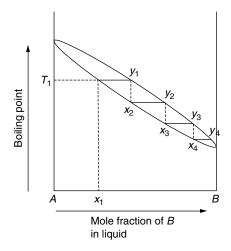
**Figure 12.1** A vapor–liquid equilibrium diagram for a hypothetical binary system of components *A* and *B*, where *B* is the more volatile (lower-boiling).

inefficient, tedious, and costly. Hypothetical pure-compound fuels would be both in very short supply and very expensive. Therefore, refining of petroleum represents a compromise between, on the one hand, the highly variable composition and properties of the world's oil supplies, and, on the other hand, the considerable expense and difficulty of separating a specific oil into its individual molecular components. Compromise is achieved by separating oil into fractions; each fraction still contains dozens or hundreds of individual components, but because the properties of the components vary only over a limited range, each fraction is of reasonably consistent nature.

# 12.1 Desalting

Sodium chloride represents the most common inorganic contaminant of petroleum, and potentially a very troublesome one. Some geological structures that collect petroleum as it migrates through the Earth include layers of salt, or are capped by salt. Saline water can infiltrate into reservoirs. During the drilling and pumping operations that are part of oil extraction, salt can get mixed with the oil. In subsequent processing, the chloride ion can form hydrochloric acid, which is corrosive to processing equipment. Therefore, the first operation in many refineries is desalting the oil.

Salt concentrations of 0.06 g/l or greater would require the oil to be desalted. In some refineries, all oils are desalted as a matter of routine. The salt is in solution in water that is emulsified with the oil. In some cases, the water may also contain suspended crystals of salt, as well as other inorganic debris, such as flakes of iron oxide rust from pipes or storage tanks. The general approach is to mix the oil with water, and heat it to a temperature that will produce a water-and-oil emulsion, using enough applied pressure to keep the water in the liquid state. The volume of water used is about 3–15% of the volume of the oil. The exact amount of water depends on the gravity of the oil. As examples, for crudes greater than 40° API, about 3–4% of water would be used. Heavier oils, say <30° API, would use 7–10% water. The temperature employed also depends on the oil; a 40° gravity oil and water mixture would be heated to 115–125 °C, whereas the mixture of heavier oil with water oil with water would go to about 140–150 °C.



**Figure 12.2** Successive changes in the composition of liquid and vapor of the hypothetical A-B system effected by fractional distillation; with enough steps it would be possible to produce pure A and pure B.

The intent is to dissolve salt in the added water in the course of forming a water-oil emulsion. Then, when the emulsion is "broken," the water layer, which now contains the salt, can be separated from the oil. The simple approach to separating the emulsion is just to give it time to settle. Allowing the emulsion to flow through a bed of small gravel or sand facilitates coalescence of water droplets. If physical settling is not quick enough, or not complete, various compounds can be added to facilitate separation, examples being long-chain alcohols or fatty acids. Strong electric fields have also been used for breaking the oil-water emulsions.

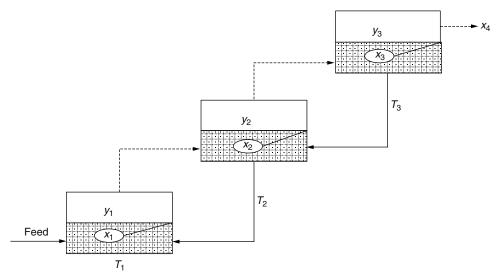
# 12.2 Principles of distillation

The essence of distillation is vapor-liquid equilibrium. When a liquid containing two (or more) components is heated, the composition of the vapor is different from that of the liquid. The vapor is enriched in the more volatile component(s). Withdrawing the vapor from the system and condensing it produces a new liquid phase with a higher proportion of the more volatile component(s) than was in the original liquid. This provides a means of separating a mixture of liquids based on the relative volatilities of its components.

A two-component liquid mixture suffices to illustrate the principles. Liquids having a greater number of components behave in the same way, though analysis of the problem becomes more complex. Referring to the components arbitrarily as the ever-useful A and B, the relationships between vapor composition, liquid composition, and temperature can be illustrated by Figure 12.1.

At any given temperature, the equilibrium compositions of vapor and liquid are different. This can be illustrated by Figure 12.2.

When an A-B mixture with composition  $x_1$  is heated to its boiling point,  $T_1$ , the vapor at equilibrium is richer in B, the more volatile of the two components. The liquid is



**Figure 12.3** A fractional distillation process. Vapors are designated by the symbol y and broken lines; liquids, by solid lines and the symbol x.

richer in A. If the vapor, which has the composition represented by  $y_1$ , is removed from the system and condensed, that newly condensed liquid has composition  $x_2$ , and is richer in B than was the original liquid. If the new liquid of composition  $x_2$  is heated to  $T_2$ , a vapor of composition  $y_2$  even further enriched in B is produced. Continuing the sequence of removing the vapor, reheating, and condensing eventually yields a liquid that is pure B. At the same time that the vapor has been becoming increasingly rich in B, the residual liquid has similarly experienced a steady increase in A. So, this sequence of steps applied to a mixture of A and B separates the mixture into pure A and pure B. In addition, as liquids become increasingly enriched in the more volatile B, they boil at successively lower temperatures.

This conceptual sequence of steps, which forms the essence of fractional distillation, could be carried out in a series of connected process vessels, as illustrated in Figure 12.3.

In the sequence shown in Figure 12.3, the liquid to be subjected to fractional distillation has composition  $x_1$ . Heat is supplied to Vessel 1 so that the liquid boils. Vapor, of composition  $y_1$ , passes into Vessel 2. Since  $T_1 > T_2$ , at equilibrium Vessel 2 contains liquid of composition  $x_2$  and vapor of composition  $y_2$ . The same argument applies to a third stage, where  $T_2 > T_3$ , and the liquid and vapor have compositions  $x_3$  and  $y_3$ , respectively.

Successive enrichment of the vapors in component B proceeds from stage 1 through 2, 3, and on through as many stages as are used. Enrichment of the residual liquid in A proceeds in reverse, being lowest in the final stage and increasing in stages 3 to 2 and finally to 1. Ideally heat would be supplied only to vessel 1, the heat for the subsequent stages being obtained from the vapor from the previous step.

Recycling some of the product from a given stage to the previous stage helps to enhance the efficiency of separation. For example, liquid of composition  $x_4$  would be recycled to stage 3, of composition  $x_3$  to stage 2, and so on. The ratio of the number of moles of material recycled to the number of moles removed in a given stage defines the

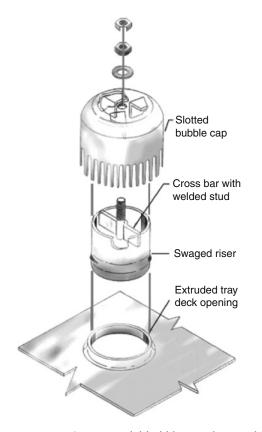


Figure 12.4 A commercial bubble cap plate used in a distillation column.

reflux ratio. Maximum efficiency corresponds to an infinite reflux ratio, corresponding to a situation in which the amount removed in a given stage is zero. This is seldom useful in industrial practice.

Although the equipment layout depicted in Figure 12.3 could be used for fractional distillation, the common industrial approach is to carry out the entire operation in a single vessel, rather than in separate units. A distillation column, or distillation tower, is a vertical, cylindrical steel vessel. The individual distillation stages, represented by separate vessels in Figure 12.3, are carried out on plates, or trays, inside the column. Each plate provides a site for bringing liquid and vapor into contact. Many different designs of plate exist; Figure 12.4 shows one example, the bubble cap plate.

The trays must be designed to provide a high degree of vapor-liquid contact, to assure approaching equilibrium between the two phases. It must do this while causing minimal pressure drop through the column and adequate liquid flow paths downward.

A distillation column affords much greater simplicity of construction and operation than would the sequence of individual units shown in Figure 12.3. However, equilibrium is never truly reached on each plate. Usually the separation attained on each plate is  $\approx 80-90\%$  of the theoretical separation at equilibrium.

On each tray, equilibrium is established between the liquid condensate coming from the tray above, and vapor rising from the tray below. Temperature decreases in the direction of flow of vapor, so that the minimum temperature occurs where the final vapor (either pure B, or whatever A-B mixture enriched in B is the desired product of the distillation) exits the column. Then, temperature must increase in the direction of flow of liquid, and would be a maximum where the final liquid is taken off.

Separation of a two-component mixture by distillation is usually straightforward, assuming that the components form an ideal solution [B] with no complicating factors such as the formation of azeotropes. If there were some reason to do so, the original mixture of A and B could be concentrated into fractions of higher amounts of A, and another with higher amounts of B, rather than distilling to pure A and pure B. As an example, a mixture containing 50% each of A and B could be used to make a product of 80% B and another of 80% A.

By extension, a mixture of, say, five components having ideal solution behavior, could be separated sequentially into the components A, B, C, D, and E by applying the same concepts. In practice, the fractional distillation of a mixture of n components into the various pure components would require n-1 fractional distillation columns. (This requirement does not apply if the intent is simply to separate into pseudo-components, as e.g., a light fraction and a heavy fraction.) This will work provided that several criteria are met. First, the components must have appreciable differences in volatility. Second, the mixture must be an ideal solution. Third, no chemical reactions between the components should occur under the conditions of distillation. Fourth, the components of the mixture must be able to vaporize at temperatures and pressures that can be attained in practical laboratory or refinery operation.

Unfortunately, problems arise and multiply rapidly when distilling a material like petroleum, with tens of thousands of components. In distillation theory, petroleum is classified as a complex system, which has several implications. The designation "complex system" indicates that the system is composed of such a large number of components that it is not feasible to identify all of them individually, or to express the composition of the mixture in terms of pure components. Because both the number of individual components and their identities are not known, it is not possible to carry out a quantitative evaluation, or an engineering design, on the basis of the fundamental physical properties – such as boiling point or vapor pressure – of the pure components. Basically, there is no practical way to fractionate petroleum into its individual components.

Theoretical and practical limitations are dealt with by considering a complex system, such as petroleum, to be composed of a number of pseudo-components, or "cuts." Each cut can be characterized by average values of such properties as boiling point, API gravity, and molecular weight. The characteristics and specifications of these cuts are commonly based on various empirical tests, which can give very useful information about each cut, but cannot be used as input variables for calculating designs of distillation equipment. This process greatly simplifies cost and complexity of distilling petroleum, but it carries a penalty in that products removed from the distillation column might overlap with respect to distillation ranges. That is, there is no exact separation. What is needed and expected in a practical distillation system is: the ability to produce the desired quality of products (i.e. to effect the necessary separations into cuts); to produce a product of consistent quality; a system designed and built large enough to be capable of handling the quantity of material needing to be distilled; and,

ideally, a design that has enough flexibility to operate with occasional fluctuations in the amount of oil needing to be distilled.

Criteria or indicators are needed to specify whether a particular separation is, or is not, a good one. One such approach compares the temperatures at which 95% of the lighter product, and at which 5% of the heavier product have distilled. A temperature difference can be calculated as

$$\Delta T = 5\%_{\rm vol}T_H - 95\%_{\rm vol}T_{\rm L},$$

where  $5\%_{vol}T_{\rm H}$  is the distillation temperature at which 5 vol% of the heavier product has distilled, and  $95\%_{vol}T_{\rm L}$  at which 95 vol% of the lighter product has distilled. If  $\Delta T > 0$ , it is referred to as a gap, and indicates that the separation between the light and heavy products is good. Alternatively, a  $\Delta T < 0$  is an overlap, indicating poor separation between the fractions.

## 12.3 Refinery distillation operations

#### 12.3.1 Atmospheric-pressure distillation

Fractional distillation of oil at atmospheric pressure is *the* primary operation in a refinery. Nothing else happens without this step occurring first. The feed, which normally will have been desalted upstream of distillation, is heated by allowing it to flow through piping enclosed within a furnace. The furnace plus the distillation tower itself make up a distillation unit, sometimes called a pipe still. The oil is heated to a temperature that has a value specifically selected to cause a desired fraction of the oil to vaporize. Specific details vary from refinery to refinery, and probably from one oil to another, but furnace outlet temperatures would be in the range 340–400 °C. What is now a vapor–liquid mixture is then allowed to flow into the distillation tower itself. There, the liquid descends while the vapor rises through the tower.

Partially vaporized feed enters the tower in the so-called flash zone, where no trays are located. The portion of the tower above the flash zone is called the rectifying section, and usually contains most of the trays. Here, the proportion of the less volatile components of the oil is progressively reduced as the vapors ascend the tower. The region below the flash zone is called the stripping section, because there the more volatile components are stripped out of the liquid. The temperature at the exit of the pipe still furnace is chosen so that all of the products to be taken off in the flash zone, and about 20% of the material in the rectifying section, are in the vapor phase. The highest boiling temperature for the heaviest cut that can be made by atmospheric-pressure distillation is limited by the temperature at which the feed begins to decompose thermally. Generally this upper temperature limit is around 350 °C. If further processing of the distillation residue (the residuum or "resid") is desired, this is accomplished by vacuum distillation.

Vapors leaving the top of the distillation tower enter a condenser, where pentane and heavier compounds are condensed. The liquid may contain some dissolved propane and butane. This product is light gasoline. Because a distillation tower operates as an enormous reflux condenser, some of this liquid returns to the tower as reflux. Processing of these so-called light ends involves separating the dissolved propane and butane from the remainder of the liquid. If necessary, propane and butane can be sweetened to remove hydrogen sulfide. The sweetened gases constitute the product known as liquefied petroleum gas, or more commonly by its initials LPG. The "debutanized" liquid undergoes a simple distillation, in a so-called stabilizing tower, to light naphtha, the  $C_5$  and  $C_6$ compounds, and to heavy naphtha, rich in  $C_7$  and larger alkanes and in cycloalkanes. Light naphtha is used later in the refinery for blending with other process streams as part of the gasoline pool, i.e. all of the various products in the refinery that become blended to make the gasoline sold as the final, marketable product. Heavy naphtha typically would be processed further into gasoline by catalytic reforming (Chapter 14).

A perfect separation of components cannot be achieved in a single, simple fractional distillation. Consequently, each of the cuts withdrawn from the distillation tower contains some components that are undesirable or not wanted in that particular fraction. To remedy this, each product is sent directly to a sidestream stripper. These strippers are small, atmospheric-pressure distillation units that remove the more volatile components of each of the products. A given distillation cut, or sidestream product, enters the top of the stripper, and steam is fed into the bottom. The volatile components that have been stripped out of the cut return to the main distillation tower; the stripped product exits the bottom of the stripper and proceeds to other downstream refining operations. A sidestream stripper needs to handle only a single cut from the main distillation tower, so that physically the stripper itself can be shorter and smaller than the main tower. This makes it easy to locate the strippers in a vertical stack as if they were a single distillation tower; however, each one of the individual strippers operates separately and independently of the others.

### 12.3.2 Vacuum distillation

Some refineries have markets for materials having very high boiling ranges, such as lubricating oils. To distil crude oils without extremely high temperatures that would cause cracking and carbon deposition, the pressure must be reduced. This can be done by vacuum distillation (i.e. adding a vacuum tower) to the atmospheric-pressure distillation operation. In this case, resid from the atmospheric tower would be pumped to the vacuum tower, which operates at  $\approx 2-15$  kPa. The very low pressure results in a large volume of vapor. Consequently, vacuum towers may be 15 m diameter. The furnace outlet temperature for the vacuum tower would be in the range 380–450 °C. Steam is added, to suppress formation of carbonaceous solids from thermal cracking of the feed.

The overhead from the vacuum tower is gas oil. It comes off the vacuum tower at  $\approx 150$  °C; its boiling range at atmospheric pressure is 315-425 °C. Lubricating oil ("lube oil") fractions are taken off the vacuum tower as sidestreams. Distilling some of the high-boiling materials that would be used to make lubricating oil could require pressures as low as 2–4 kPa, though it is usually possible to operate at 6–15 kPa. These cuts are taken at 250–350 °C. Vacuum tower bottoms, often called vacuum resid, serves as a source of asphalt, or can be sent to delayed coking (Chapter 16) for production of petroleum coke and light liquids. The resid temperature is kept at 350 °C, or less, to minimize thermal cracking and coke deposition.

The products of vacuum distillation depend on whether the intent is to produce lubricating oils. If so, gas oil would be processed further to make gasoline by catalytic cracking (Chapter 14), or possibly treated to make a light grade of lubricating oil. The sidestreams constitute one or more fractions of lubricating oil. The bottoms serve as a source of asphalt. If lubricating oil is not a desired product, then there could be a simpler distillation into a single liquid fraction as feed for catalytic cracking, and a resid for asphalt production.

# 12.4 Introduction to petroleum distillation products

Oils vary widely in composition, so do not all give the same distillation products, or the same proportions of products. Further, current environmental regulations – likely only to become increasingly stringent in the future – and fuel-quality requirements for modern engines make it nearly impossible to obtain marketable material directly from distillation. Essentially everything sold from a modern refinery has passed through one or more additional refining operations downstream of distillation. Though distillation is the crucial operation in a refinery, without which not much else could happen, what distillation really does is to make materials that become feedstocks for downstream refining operations.

Some of the principal products are introduced in this section, to lead into more detailed discussions in Chapters 14–16. The long and colorful history of the worldwide petroleum industry has resulted in a variety of terms coming into usage, as well as differences in distillation cut points for various fractions. This section provides examples, without intending to be a comprehensive catalog, or to cover all the possible terminology or refining parameters.

### 12.4.1 Gasoline

Petroleum as fed to the refinery can contain dissolved light hydrocarbons that would be gases at ambient conditions, such as propane and butane. They come out of solution as the oil is heated for distillation, and come off the distillation column as part of the overhead stream. They have use both as fuel gases (LPG), and for sale to the petrochemical industry. The first distillation product that is liquid at ambient conditions is gasoline. In some parts of the world, gasoline is the most important energy source or product – excepting only electricity – that people encounter and use directly. In the United States, the market demand is such that about 50% of each barrel of petroleum fed to a refinery needs to be converted to gasoline. This situation is not the same worldwide, particularly as a result of the steady "dieselization" of the vehicle fleet. In some nations nowadays half the vehicles have diesel engines, and in a few countries, well over half.

Most oils yield, at best, no more than about 20% gasoline from distillation. The considerable gap between gasoline produced directly from distillation, called straightrun gasoline, and the demand for gasoline at the refinery gate, means that refiners face a considerable challenge to produce gasoline from other petroleum fractions. The other issue affecting straight-run gasoline, aside from there not being enough to meet market demand, is its poor combustion performance in modern engines, as indicated by a low octane rating. Thus refiners have the double problem of increasing both the quantity and the quality of gasoline during refining. Properties and specifications of straight-run gasoline vary with the specific oil being processed and the type of distillation operation used. Generally, the boiling range of gasoline is 40–200 °C. This boiling range covers  $C_5$ – $C_9$  *n*-alkanes, and lighter alkylcy-cloalkanes and alkylaromatics. Some heavier compounds that have appreciable vapor pressures at  $\approx 150$  °C could also be present in straight-run gasoline.

### 12.4.2 Naphtha

Material distilling between 30 and 200 °C is referred to as full-range naphtha. Typically, light naphtha is cut at 30 to 90 °C, and the remainder constitutes heavy naphtha. By far the most important use of naphtha is as a feedstock to catalytic reforming (Chapter 14) for production of high-octane gasoline. Naphtha is also subjected to thermal cracking to produce alkenes, of which ethylene is most important. Naphtha is seldom used directly as a fuel, except for applications in liquid fuel for portable stoves used for camping, and in cigarette lighters. Naphtha is a good solvent for organic materials, such as oils or grease, that do not dissolve in water. It is sometimes sold as "petroleum naphtha" as a cleaning solvent.

### 12.4.3 Kerosene

Development of the petroleum industry in the United States was driven by the need for kerosene, for use as a fuel in lamps and lanterns. The first well, drilled by Edwin Drake near Titusville, Pennsylvania, was in a location chosen for the presence of natural oil seeps, and on the basis of an analysis of the seepage oil that indicated the likelihood of high yields of kerosene from distillation. Typically, kerosene is taken as a fraction boiling between 150 and 275 °C. In some countries it is called paraffin.

Once, kerosene was a dominant product of petroleum refining. In that era, refineries consisted of little more than a distillation unit and storage tanks for the products. Gasoline was a nuisance to be got rid of. In the late nineteenth century kerosene was widely used as an illuminant in lamps. This application alone made it the most valuable product from petroleum. In the early decades of the twentieth century, especially after World War I, new factors emerged: the spread of electrification, especially into rural areas that previously depended on kerosene for illumination; and the great increase in affordability of gasoline-fueled automobiles. Gasoline became the most important petroleum product while kerosene no longer dominated. After World War II, displacement of gasoline-fueled piston-engine aircraft with jet aircraft revived a demand for kerosene. Kerosene does not enjoy its former dominance among petroleum products, and probably never will again, but it remains important, accounting for about 10% of refinery output. Nowadays most kerosene is upgraded further to produce aviation gas turbine fuels, commonly called jet fuels.

Jet fuel is a highly refined form of kerosene. Other applications utilize kerosene of lower quality. "Power kerosene," sometimes also known as TVO, for tractor vaporizing oil, has been used as a cheap fuel for vehicles and machinery used in agriculture or industry. Kerosene used for domestic space heating, called household kerosene, must have a carefully controlled boiling range. If the boiling range is too low, vapors of the fuel building up inside the heater can explode upon ignition. This problem has occurred, for example, when household kerosene was inadvertently adulterated with gasoline [C]. On the other hand, too high a boiling range leads to poor vaporization and inefficient combustion.

For any liquid fuel, the flash point expresses the temperature at which the vapors of that liquid will ignite when exposed to an open flame. The flash point provides an indication of safety in storage and handling the fuel; the higher the flash point, the less likely that the vapors will be ignited inadvertently. Household kerosene should have a flash point of  $\approx$ 50 °C. Because the combustion products from kerosene-fired space heaters or kerosene lamps are often vented directly into a room – not that this is a recommended practice – carbon monoxide, smoke, and soot are extremely undesirable products [D]. As a rule, the higher the hydrogen content of the fuel, the cleaner is the flame. Kerosenes high in alkanes are preferred, relative to naphthenic or aromatic fuels.

#### 12.4.4 Diesel fuel

Rudolf Diesel designed his engine to operate on fuels of lesser quality and lower cost than gasoline. Remarkably, one of Diesel's early predictions was that plant-derived oils would become important fuels for his engine; it took a while, but the steadily increasing importance of biodiesel is a testament to his sagacity. It is a tribute to the accomplishments of Diesel the engineer and of the diesel engine that diesel fuel is the only product whose name derives from that of the engineer who developed the engine in which it is used. Aside from using plant oils, much of the early developmental work focused on possible fuels such as coal tars or even pulverized coal [E]. Modern diesel engines operate on a "middle distillate" fuel, so called because its boiling range is intermediate between gasoline and naphtha on the one hand and high-boiling fuel oils and resids on the other. Several grades of diesel fuel are normally marketed, defined by the temperature at which 95% of the fuel has distilled. For the more volatile No. 1 diesel, the "95% over" point is 288 °C, while for No. 2 diesel it is 355 °C.

The higher boiling range of diesel relative to gasoline indicates that larger molecules are present in the diesel. Diesel fuel contains alkanes up to eicosane, and aromatics as large as alkylated naphthalenes. Diesel fuel has a lower API gravity than gasoline, and higher viscosity. Many diesel fuels have API gravities around 35°, lower than might be expected for alkanes boiling in the diesel-fuel range; for example, hexadecane has an API gravity of 51°. The lower API gravity relative to alkanes reflects the presence of substantial quantities of aromatics.

Marine diesels, the engines used on ships, use residual diesel oil, or marine diesel fuel. This is a heavier fuel than that used in automobiles and light trucks, with API gravity of about 27°.

#### 12.4.5 Fuel oils

Some fuel oils are distillation cuts; others come from resids. They are used as heat sources, for applications such as home heating, process heat in industry, or raising steam in electric generating plants. The terminology of fuel oils is not precise. Sometimes gas oil or diesel fuel are also classified as fuel oils; fuel oils are also called heating oils. Fuel oils are graded on the basis of viscosity. To achieve a desired viscosity, a resid can be blended with a distillation cut. Fuel oils are also classified by a numerical system, in which the increasing numbers imply increasing viscosity.

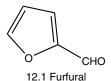
No. 1 fuel oil is comparable to kerosene. No. 2 oil is also a distillation product, very similar to No. 2 diesel fuel. The other oils are all resids (there is no No. 3 oil). The No. 5 and 6 oils are sometimes called bunker oils. They have such high viscosity that they have to be heated to be pumped through fuel lines and burner nozzles. Some bunker oils have pour points up to  $30 \,^{\circ}$ C, as compared with, e.g.  $0 \,^{\circ}$ C for marine diesel.

### 12.4.6 Lubricating oils

Lubricating oils, or "lube oils," have very high boiling ranges, and are usually produced by vacuum distillation. The overhead from the vacuum tower is gas oil. Lube oils are taken off as sidestreams. The vacuum bottoms are asphalt. Lube oil could consist of: 20–25% alkanes, both straight- and branched-chain; 45–50% cycloalkanes of one to three rings, possibly with alkyl side chains; 25% alkylated hydroaromatic compounds of two to four rings; and 10% high molecular weight aromatics. Lube oils might amount to  $\approx 2\%$  of the total petroleum processed, but their high selling price makes them desirable products. An enormous array of products, numbering into the thousands, is sold for lubrication applications.

Four characteristics are desirable for lube oils. High-temperature stability helps the oil resist degradation from heat generated by the friction of the parts the oil is supposed to be lubricating. Low-temperature fluidity ensures that the oil will flow between moving parts even at low temperatures, such as when starting an engine in the winter. Adhesiveness assures that the oil molecules will cling to the metal surfaces even under very high shear rates. The effect of temperature on viscosity should be minimal, so that fluidity of the oil will be nearly the same from a cold start up to high temperatures that might be generated by high-speed operation. Long-chain alkanes provide most of these properties.

If simple vacuum distillation is not adequate to provide good-quality lube oil, solvent extraction with furfural (12.1)



dissolves aromatics, cycloalkanes, and NSOs. NSOs can be removed by clay treatment. Clay absorbs the NSOs via electrostatic interactions between the polar NSOs and the surface of the clay.

When lubricating applications call for a material of viscosity even higher than a lube oil, semi-solid lubricants called greases can be used. Usually grease is made by blending lube oil with a so-called metallic soap, a salt of fatty acids with a multivalent cation such as aluminum, calcium, or zinc.

## 12.4.7 Waxes

Alkane molecules in waxes have 18–56 carbon atoms. Waxes are moderately hard, brittle solids at room temperature, generally melting in the range 50–60 °C. The dominant market for wax is the food industry, for impregnation of paper and cardboard for food preservation. The original market, which still exists, was manufacture of

candles. The related petrolatums are semi-solid materials at room temperature (sometimes called petroleum jelly), having a broad melting range ( $\approx$ 40–80 °C). They find use in the pharmaceutical and cosmetic industries, sold under various brand names for softening and lubricating skin.

Waxes can also be useful feedstocks for the chemical industry. Thermal cracking of waxes at 540–565 °C, 0.2–0.4 MPa, and 5–15 s residence time produces 1-alkenes in the C<sub>6</sub>–C<sub>20</sub> range [F]. Wax cracking is a  $\beta$ -bond scission process. Unzipping, which involves a succession of  $\beta$ -bond scissions, produces very high yields of ethylene. Cracking for ethylene production is done at much higher temperatures (750–900 °C), which increases endothermic bond breaking.

## 12.4.8 Asphalt

Asphalts are mixtures of aromatics, long-chain alkanes, and high molecular weight NSOs. Asphalts can have pour points exceeding 95 °C. Vacuum resids provide a good source of asphalt. Treating resid with liquid propane at 70 °C and 3.5 MPa dissolves all of its components except the asphalt. Once the asphalt has been separated, reducing the pressure lets the propane evaporate, yielding a product called residual lube oil. Residual lube oil can be upgraded by an appropriate combination of solvent extraction, dewaxing, and clay treatment.

Deasphalting vacuum resid can serve different purposes. On the one hand, deasphalting can be used to make asphalt as a marketable product, such as for road paving. Alternatively, the process can be used to remove asphaltenes that would contribute to coke formation on catalysts in downstream processing of the deasphalted oil (Chapter 13).

### Notes

- [A] Native Americans used petroleum as a medicine, which might actually work for the highly paraffinic Penn-grade crudes. A product called mineral oil, liquid paraffin, or paraffin oil is available under numerous trade names and has been used as a laxative and a purgative. It is a mixture of various alkanes, probably not much different from the best-quality Penn-grade crude.
- [B] An ideal solution is one in which intermolecular interactions are completely uniform. For the famous two-component mixture A and B, this means that forces between A and A molecules, between A and B molecules, and between B and B molecules are all the same. Its importance in distillation is that the tendency of a given molecule of, say, A to escape from the liquid into the vapor phase is exactly the same regardless of whether that particular molecule happens to be surrounded entirely by other molecules of A, or surrounded by B molecules, or surrounded by a mixture of A and B molecules.
- [C] A tragic case resulted when a service station had underground gasoline and kerosene storage tanks connected into a common vent stack without check valves to prevent condensed vapors from running back into the tanks. Low local demand for kerosene meant that the kerosene tank was seldom refilled and often allowed to be nearly empty. Gasoline vapors condensing in the common vent ran back into the

kerosene tank, so that the kerosene was steadily enriched in gasoline. Eventually a customer bought some of this "kerosene" for her home space heater. The resulting explosion and fire took the life of her daughter, who was at home asleep at the time.

- [D] Everyone should be aware that carbon monoxide is lethal. Installing carbon monoxide detectors in any dwelling in which any fuel is burned indoors is cheap but effective life insurance.
- [E] A comment was once made during a review of coal development and demonstration programs that, "Not only is the use of pulverized coal in diesel engines an idea whose time has passed, it is an idea whose time should never have come in the first place." Trying to use pulverized, but solid, coal was not one of Diesel's better ideas.
- [F] Industrially, these compounds are known as  $\alpha$ -olefins. They range from 1-hexene up to about 1-octadecene, and have a variety of important industrial applications, such as in the synthesis of polymers, of detergents, and of synthetic lubricating oils. Shorter alkenes, ethylene through 1-butene, enjoy enormous importance in the polymer industry, with ethylene itself being *the* most important industrial organic chemical.

#### **Recommended reading**

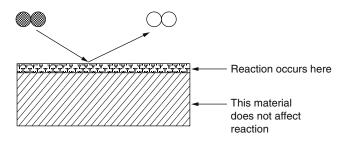
- Atkins, Peter. *Physical Chemistry*. W.H. Freeman: New York, 1998. Most textbooks of physical chemistry have a section or chapter devoted to vapor-liquid equilibrium. This book is an excellent physical chemistry text; Chapter 8 is particularly relevant.
- Gary, J.J. and Handwerk, G.E. *Petroleum Refining*. Marcel Dekker: New York, 1984. A comprehensive book on refinery processes. Chapter 4 covers distillation.
- Mujtaba, I.M. *Batch Distillation Design and Operation*. Imperial College Press: London, 2004. Much useful information on distillation concepts and processes.
- Sinnott, Ray. *Chemical Engineering Design*. Elsevier: Amsterdam, 2005. A classic textbook in its field; Chapter 11 provides substantial information on distillation operations.
- Speight, James G. *The Chemistry and Technology of Petroleum*. Marcel Dekker: New York, 1991. Chapter 13 of this useful, very comprehensive treatise deals with distillation processes.
- Van Winkle, Matthew. *Distillation*. McGraw-Hill: New York, 1967. This book covers the principles of distillation and design of distillation equipment (albeit from an era when computers were a luxury) in a very readable manner. It does not concentrate solely on petroleum.

In practical industrial processing, reactions must take place on time scales reasonably short from a human perspective – ideally in units of hours, at the most. Compared to natural geological processes, reaction times need to be reduced by up to ten orders of magnitude. Two approaches can do this. One is to increase reaction severity, usually increasing temperature. As a rough rule, reaction rate doubles for every 10 K increase in temperature. The highest temperature encountered in fuel formation is  $\approx 225 \,^{\circ}$ C, the closing of the gas window or the fourth coalification jump. Temperatures of fuel processing are often much higher, and reaction rates are correspondingly higher. The second approach is to use a catalyst to enhance reaction rate. Of course, in many situations both strategies are used together.

A catalyst changes the rate, outcome, or both, of a reaction without appearing in the net equation for the reaction (i.e. without being consumed in the reaction, or being permanently altered by the reaction). Although catalysts often find use to enhance rate, sometimes they are used to arrive at a different set of products. This is very important in, e.g., the production of high-quality gasoline (Chapter 14). As materials, catalysts are of extreme importance. Virtually all biochemical processes in living organisms are catalyzed by enzymes. About 90% of the fuels, synthetic chemicals, and plastics produced by the chemical industry have benefited from a catalyst in at least one of their processing steps.

Chapter 2 introduced the concept of catalysis, and focused on homogeneous catalysis. For large-scale production of commodities such as fuels, a homogeneous catalyst requires separation and recovery steps downstream of the reactor, unless the catalyst either is thrown away or is allowed to dilute or contaminate the product. This adds to the complexity and expense of a process. Heterogeneous catalysts are favored by industry, especially for production of commodities. In part, this derives from a very easy, even non-existent, separation from the process stream. Many heterogeneous catalysts can withstand more severe conditions of temperature and pressure than homogeneous catalysts, especially enzymes. Heterogeneous catalysts work well for gas-phase reactions, where it might be difficult to select a homogeneous catalyst [A].

Several criteria must be fulfilled by any heterogeneous catalyst used in industrial processing. It must provide a rate of reaction high enough to achieve conversions needed for a commercially viable process. It should show good selectivity, which means that it should induce formation of desired products and suppress, or at least not enhance, formation of those that are not desired. The catalyst must have sufficient stability to withstand temperatures, pressures, and mechanical stresses in the reactors in which it is likely to be employed.



**Figure 13.1** Heterogeneous catalysis occurs on the surfaces of catalyst particles. That portion of the catalyst particle that is not exposed to reactants does not participate in the reaction.

## 13.1 Catalytic materials

### 13.1.1 The active species

In fuel chemistry, the kinds of reaction for which catalysts are most often used are shuttling hydrogen into or out of molecules, changing the size of molecules by cracking large ones or putting together small ones, or changing the shapes of molecules through carbocation rearrangement. Metals tend to be good catalysts for hydrogenation and dehydrogenation. In some processes, metal sulfides can be useful, especially when the process stream is contaminated with sulfur. (Sulfides tend to resist side reactions with sulfur much more than do other materials.) For generating carbocations, metal oxides are preferred. But, there is no such thing as a "universal catalyst." Just because a substance catalyzes one particular type of reaction it does not mean that it will catalyze *all* reactions. Further, within a given class of catalysts, and a given reaction to be catalyzed, "not all catalysts are created equal." There is a considerable difference in activity among different catalysts selected for the same application.

Good catalysts for hydrogenation are metals at the end of the transition series: iron, cobalt, and nickel; ruthenium, rhodium, and palladium; and osmium, iridium and platinum. How these elements catalyze hydrogenation reactions is discussed below. Of these, platinum and palladium are best. In many applications nickel might be used instead, because of its much lower cost. In very high-tonnage applications, iron might be chosen because it is cheaper still. Nevertheless, platinum, palladium, and their alloys are frequently selected for hydrogenation applications. These are rare, expensive metals, and our ability to use them on an industrial scale depends on dispersing them onto a much less expensive material, the catalyst support.

#### 13.1.2 The support

The key to using a very expensive material such as platinum, or even a moderately expensive one such as nickel, in large-scale industrial processing derives from the nature of heterogeneous catalysis: because the catalyst, by definition, is in a separate physical phase from the reactants and products, all of the chemical processes occur on the surface, as sketched in Figure 13.1.

Only the surface layer needs to be catalytically active. The remainder of the catalyst can be some other material, ideally much cheaper than the catalytically active species.

The nature of the surface is critical for catalysis, but the bulk of the material, which does not interact with reactants or products, has no effect on the chemistry. Since reaction occurs only at the surface, the composition of the bulk of the catalyst particle is immaterial. Only when the catalyst is relatively inexpensive, the fact that the bulk of the material may not participate in the catalytic reaction has little importance.

The solid used to provide the bulk of the catalyst particle, and the underpinning for the catalytically active surface, is called the catalyst support. A satisfactory catalyst support must fulfill several criteria. It must have physical and mechanical integrity to resist the temperature, pressure, and stresses encountered in the reactor. It should interact enough with the catalytically active species to provide good physical dispersion and mechanical support, but should not react to the extent of degrading performance of the catalyst itself. The support should not itself catalyze some other, undesired reaction. The support should have adequate surface area and porosity to provide facile reaction with little or no diffusion resistance in the pores. And, ideally, the support should be relatively inexpensive. The choice of support is often a refractory oxide. Choices include silica, alumina, and various aluminosilicates such as mullite or zeolites. Carbon is another potentially useful catalyst support.

The importance of the pores in the catalyst or its support derives from several factors. Pores can enhance (sometimes substantially) the total surface area available for the reaction. To the extent that reaction rate is proportional to surface area, this can increase the rate substantially. The distribution of pore sizes can also affect the course or outcome of a reaction. As an example, if it were desired to react selectively the small molecules in a complex mixture, it might be advantageous to use a microporous catalyst, since large molecules would have difficulty penetrating the micropores. Alternatively, if the reactant consisted of large molecules, a macroporous catalyst might be preferred. Measurement of porosity is discussed later in this chapter.

Other physical and mechanical properties are also important. Hardness affects catalyst use in two ways. In a fixed-bed reactor, catalyst pellets should be rigid, to resist breaking down to produce fines. Over time, that breakdown could be nearly as bad as charging the reactor with fines in the first place. In fluid-bed reactors, catalyst powder should not be abrasive or erosive, in which case the catalyst particles could effectively "sand blast" reactor internals. Because many catalytic processes are hightemperature reactions, ability to withstand high temperatures is important. At high temperatures the pore walls might fuse, which can affect the apparent activity of the catalyst by reducing surface area. In a fluidized-bed reactor, thermally induced agglomeration or sintering can cause particle size to grow to a point at which the catalyst particles can no longer be fluidized in the gas stream. Fluidization is lost (the bed "slumps"), the reaction slows or stops, and pressure drops across the bed become unacceptably high. An extreme case could involve outright melting of the catalyst. The nominal reaction temperature is not the only consideration. If the desired catalytic reaction is exothermic, it is possible to develop localized "hot spots" that could collapse pores or cause sintering. Thermal conductivity must be taken into account, especially in large reactors. If the reaction is highly exothermic, heat must be conducted out of the reactor to avoid thermal degradation of the catalyst or runaway reactions. On the other hand, if the reaction is highly endothermic it is necessary to get heat into the reactor without grossly overheating the catalyst near the reactor walls.

### 13.1.3 The promoter

Some substances that may not be catalytically active themselves can nevertheless enhance the performance of a catalyst. These substances are called promoters. A catalyst promoter is any substance that, when added to the catalyst in small amounts, improves one or more properties of the catalyst. Promoters are used to improve activity, selectivity, lifetime (the time on stream before the catalyst has to be regenerated or discarded), or some combination of these properties.

Many promoters, especially for metal or oxide catalysts, are the strongly electropositive elements or their cations. A good example is potassium oxide, or the potassium cation. Though many substances can be, indeed have been, used as catalyst promoters, if in doubt potassium oxide is almost always a good choice. Promoters of this kind work by generating a partial positive charge at the surface of the catalyst, which interacts with molecular orbitals in the reactant species, reducing the energy of the orbital and facilitating interchange of electrons with the catalyst surface. For metal sulfide catalysts, promoters may be non-stoichiometric sulfides of other transition metals, such as  $Co_9S_8$ . These promoters facilitate formation of surface defects that can serve as the catalytically active sites in a catalyst such as  $MoS_2$ .

### 13.1.4 Preparation

In selecting a catalyst, factors to be considered include the nature of the catalytically active species, the nature of the support, the form of the catalyst (which is dictated by the kind of reactor used), surface area and porosity, mechanical strength, abrasiveness, thermal behavior, and the choice of a promoter, if one is to be used.

Unfortunately, the common catalytically active species – metals, metal oxides, and metal sulfides – are ordinarily not soluble in water or other common solvents. To get around this problem, preparation of a supported catalyst begins with a soluble salt of the catalytically active metal. For platinum, as an example, the precursor salt could be potassium hexachloroplatinate,  $K_2PtCl_6$ . The porous support is impregnated with a solution of the precursor, and dried. Calcining, which may be done sequentially with drying or concurrently, converts the precursor usually to an oxide form, e.g.

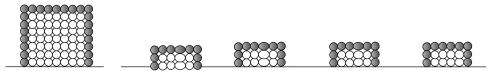
$$K_2PtCl_6 + 2H_2O \rightarrow 2KCl + 4HCl + PtO_2.$$

Any residual potassium salts can be removed by washing. Activating the catalyst then involves (usually) reducing it in hydrogen, e.g.

$$PtO_2 + 2H_2 \rightarrow Pt + 2H_2O.$$

The conditions of the reduction or activation process are chosen to provide the desired dispersion of Pt on the support.

In applications dealing with process streams containing sulfur compounds, it can be advantageous to convert the catalyst to a sulfide form before reaction, i.e. pre-sulfiding the catalyst. Numerous recipes exist for pre-sulfiding, but all involve heating the catalyst with a volatile sulfur-containing compound and hydrogen. Sulfur compounds that could be used include dimethyl sulfoxide, methanethiol (methyl mercaptan), dimethyl sulfide, or dimethyl disulfide. Often the sulfur compound is introduced to the catalyst at 175-200 °C, and the system then heated to 260-300 °C. The active



**Figure 13.2** Reducing the size of catalyst particles increases the proportion of catalyst atoms (represented by shaded circles) in the system that are accessible to the reactants. The single catalyst particle on the left contains 72 atoms, of which 23 are on the surface. Dividing the particle into four smaller ones, on the right, retains the same 72 atoms, but now 40 are on surfaces.

sulfiding agent is hydrogen sulfide, which forms in this reaction system. The sulfiding process proceeds for several hours, depending on the amount of catalyst to be treated.

Preparation of sulfide catalysts, of which  $MoS_2$  serves as an example, begins with impregnation of a support, such as alumina, with a solution of the heptamolybdate anion,  $Mo_7O_{24}^{-6}$ . The amount of molybdenum is adjusted to obtain a monolayer of molybdenum on the support. Salts of cobalt or nickel can be added during this process, as promoters. In such cases, the resulting catalysts are commonly referred to as "CoMo" or "NiMo" catalysts, though these formulas do not imply that the catalyst is an alloy or intermetallic compound of the two elements. Reaction of the impregnated support with a mixture of hydrogen and hydrogen sulfide, or hydrogen and an organic sulfur compound, sulfides the catalyst to produce  $MoS_2$  on the surface, e.g.

$$(NH_4)_6Mo_7O_{24} + 14H_2S + 7H_2 \rightarrow 6NH_3 + 7MoS_2 + 24H_2O.$$

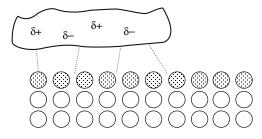
The surface of the catalytically active species available to the reactants depends on the surface area of the support. Less catalyst can be put onto the available surface area in a non-porous support than could be done for a highly porous support. Also, the size of particles or clusters of active catalyst on the support must be considered. This number is related to the relative proportions of surface and bulk atoms. With comparatively small catalyst particles, a higher proportion of atoms on the surface can be obtained, as shown in the cartoon sketch of Figure 13.2.

This concept is developed and expressed numerically, as dispersion, the percentage of atoms on the surface to the total number of atoms. As a rule, the particle size and proportion of surface atoms are inversely related (Figure 13.2).

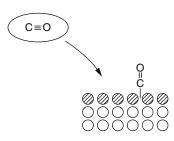
# **13.2** Adsorption on catalyst surfaces

Because heterogeneous catalysts are in a separate phase from reactants and products, the important phenomena of catalysis occur at the surface. Regardless of whether the catalyst is a metal, an ionic solid such as an oxide or sulfide, or a covalent solid such as carbon, any atoms *other than the surface layer* have all of their bonding or valences satisfied by their nearest neighbor atoms. But, the atoms in the surface layer cannot have all their valences satisfied because, necessarily (since they are the surface!) there are no atoms on top of them. The surface atoms are in a higher energy state than the atoms in the bulk, and can interact with molecules in the fluid phase surrounding the catalyst.

This interaction has two forms. One is a dipole or London-force interaction between molecules in the fluid phase and the catalyst surface (Figure 13.3).



**Figure 13.3** Physical adsorption on the catalyst surface often involves interaction of permanent or temporary dipoles in the reactant with the surface.



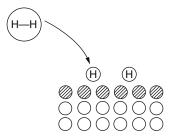
**Figure 13.4** Chemisorption of a carbon monoxide molecule on a catalyst surface involves a bonding interaction between the carbon monoxide and the surface, much stronger than the dipole interactions depicted in Figure 13.3.

In this form of adsorption onto the catalyst surface, no chemical bonds are formed or broken. The process is a physical adsorption, or as it is more commonly called, physisorption. Dipole interactions and London forces are quite weak compared to covalent bonds. The energetics of physisorption are low. Since little energy is released in physisorption, correspondingly little energy is required to reverse the process. And, since no chemical bonds have broken or formed, the adsorbed species is released intact.

In a second kind of adsorption, chemical bonds are formed between the adsorbed species and the catalyst surface. As an example, carbon monoxide can adsorb on metal surfaces with the formation of a relatively strong carbon–metal bond, as illustrated in Figure 13.4.

This situation represents chemical adsorption, or chemisorption. In some instances of chemisorption, the adsorbed molecules split apart (Figure 13.5), a process known as dissociative chemisorption. By far the most important example in fuel chemistry is dissociative chemisorption of  $H_2$ , which breaks the strong H–H bond to produce hydrogen atoms on the catalyst surface. Since chemisorption involves breaking and/or making of chemical bonds, the energy release is correspondingly greater than in physisorption. A much higher energy input would be needed to remove this adsorbed chemical species from the catalyst surface. Since bonds have been broken or made, the species that comes off the catalyst might not be the same as the one that chemisorbed onto it.

At any given time, adsorption is a dynamic equilibrium, in which some species are adsorbing on the surface while others are desorbing. At equilibrium, the rate of adsorption must necessarily equal the rate of desorption. Several factors affect the rate of adsorption: partial pressure, p, of the gas being adsorbed; the rate constant for



**Figure 13.5** Dissociative chemisorption of a diatomic hydrogen molecule results in breaking of the H–H bond.

adsorption,  $k_a$ ; and the number of sites where adsorption can take place. After adsorption starts, not all the surface remains available for adsorption, because a fraction of the surface is already occupied by adsorbed species. If there is a total of N sites on the surface, and  $\theta$  is the fraction of surface sites covered, the number of sites where adsorption can take place is  $N(1-\theta)$ . The rate at which the surface is being covered by adsorption,  $d\theta/dt$ , is then given by

$$\mathrm{d}\theta/\mathrm{d}t = k_{\mathrm{a}} p N(1-\theta).$$

Desorption can occur only from sites on the surface that are already occupied. Thus the rate at which the fraction of sites that are covered changes as a result of desorption depends only on the fraction already covered,  $N\theta$ , and the rate constant for desorption,  $k_d$ ,

$$\mathrm{d}\theta/\mathrm{d}t = -k_\mathrm{d}N\theta.$$

Since the rates are equal at equilibrium, these expressions can be set equal to each other:

$$k_{\rm a} p N(1-\theta) = -k_{\rm d} N\theta.$$

This expression is customarily solved for  $\theta$ ; usually it is convenient to use a single symbol, *K*, to represent the ratio of the two rate constants  $k_a/k_d$ . Doing so gives as a final result

$$\theta = K p / (1 + K p).$$

This equation is called the Langmuir (Figure 13.6) isotherm [B] and is one of the most common, and one of the most important, descriptions of gaseous adsorption.

The Langmuir isotherm usually plots  $\theta$  as some function of p, or some measure of p. This can be done in various ways, but one approach is to show a plot of  $\theta$  vs. p. The resulting curve starts at the origin, because if there is no gas at all (i.e. if p = 0) then there can be no surface adsorption. At low values of gas pressure, coverage of the surface as a function of pressure is linear. In essence, as we introduce more molecules of gas into the system, there are more opportunities for those molecules to strike the catalyst surface and stick there. But, as p (and therefore  $\theta$ ) continue to increase, fewer and fewer surface sites remain available for new adsorption to take place. Therefore, it is progressively more difficult to adsorb more species. In turn, this causes a slope change in the graph, i.e. causes the curve to "bend over." The limit for adsorption occurs when the surface is totally covered. This is called saturation, and at that point  $\theta = 1$ . Thus the adsorption isotherm asymptotically approaches  $\theta = 1$ , see Figure 13.7.



Figure 13.6 Irving Langmuir, who contributed enormously to our understanding of surface phenomena and catalysis.

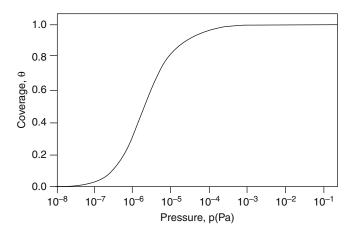


Figure 13.7 An example of a Langmuir isotherm for adsorption.

The Langmuir approach is based on a number of assumptions: monolayer coverage on the surface, no interactions among the adsorbed atoms (sometimes called lateral forces), constant heat of adsorption,  $\Delta H_a$ , as a function of  $\theta$ , and all adsorption sites are equivalent. Though these conditions are rarely met in practice, the Langmuir isotherm is nonetheless often very useful in understanding adsorption behavior on catalysts, and in other applications, such as adsorption onto carbons.

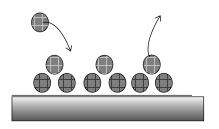
On an external surface, or inside the larger-diameter pores, additional adsorption can occur on top of the first layer of adsorbed species. Unless completely non-reactive species adsorb, it is questionable whether the adsorbed atoms or molecules fail to interact, especially for species that are chemisorbed. Indeed, when two gases are adsorbing at once, with the idea of getting them to react, such as the case of CO and  $H_2$  (Chapter 21), then they must violate the Langmuir assumption that no interaction occurs between adsorbed species.

Whether  $\Delta H_a$  is constant may or may not be the case. For example, when a surface is partially covered with a strongly chemisorbed species, e.g. carbon monoxide on nickel, there might be a chemical bond between the adsorbed species and surface atoms, and there could be a redistribution of energy states in the surface such that the heat of adsorption on the remaining, uncovered surfaces is changed. Except for a surface perfectly smooth at the atomic scale, on a perfectly pure non-porous solid, it is not likely that all surface sites would be equivalent. Surfaces at the atomic scale may have a significant amount of roughness; possibly, the atomic arrangement on some sites could be different from that on other parts of the surface. Therefore the surface energies can be different. For catalysts that are not a single, pure elemental substance, such as a metal oxide, the metal-atom surface sites are different from oxygen-atom sites.

Situations in which there are no lateral forces are rare. A consequence of the existence of lateral forces is that heat of adsorption depends on the extent of adsorption that has already occurred, i.e. on the surface coverage. If  $\Delta H_a$  depends on coverage, the equilibrium constant must do so also. Generally  $\Delta H_a$  (and, by extension, the equilibrium constant) decreases as  $\theta$  increases. A practical system in which this is important is oxidation of carbon monoxide on palladium or platinum, as occurs in the catalytic converters of vehicle exhaust systems.

It is also assumed that a molecule or atom interacting with an adsorption site on the surface is either adsorbed or not. The solid surface has sites where the incoming reactant molecule can interact and bond, i.e. stick to the surface. The sticking coefficient expresses the probability of a molecule sticking to the clean surface of the solid. Thus the rate of adsorption is determined by the gas pressure, the fraction of the surface not yet covered or blocked by adsorbed molecules, the rate of collisions per unit surface area, and the sticking coefficient. Furthermore, we implicitly assumed that the molecule or atom being adsorbed arrived from the gas phase. In many adsorption processes, the first step is physisorption, regardless of whether chemisorption follows. That being the case, nothing necessarily prohibits the initial physisorption from occurring onto the monolayer – or partial monolayer – chemisorbed to the actual catalyst surface. This weakly held, physisorbed species can diffuse on the surface formed by adsorbed material, until it finds an appropriate site on the actual catalyst surface where it can attach. In the ideal Langmuir case, the sticking coefficient would relate directly to surface coverage. However, considerable deviations can be expected, depending on how these so-called precursor states form. If the precursor state forms and either quickly finds a surface site or not, the deviation is small. On the other hand, if the precursor state allows for physisorbed species to "hunt" for an adsorption site on the catalyst surface, then there can be high sticking coefficients even at fairly high surface coverage.

The Langmuir isotherm serves as a useful model for ideal adsorption onto ideal solids. Because the world is not ideal, various alternatives to the Langmuir approach have been proposed. They differ in degree of mathematical sophistication, aimed at addressing one or more of the perceived shortcomings of the Langmuir model. One of the most successful is the Brunauer–Emmett–Teller [C] model, almost universally known as the BET model. The important distinction of the BET model, relative to Langmuir, is its incorporation of multilayer adsorption. The fact that the BET model is



**Figure 13.8** In the BET model a second layer of molecules, depicted with light shading, can adsorb onto, or desorb from, an existing layer of adsorbed molecules, depicted with darker shading.

widely used and is applied successfully in many cases suggests that indeed adsorption is often multilayer.

The BET model, like the Langmuir model, assumes that the rate of adsorption from the base surface is equal to the rate of desorption. But then each adsorbed species present on the surface of the catalyst can function as an adsorption site to start the second layer, see Figure 13.8.

This behavior implies that adsorption can keep on going essentially indefinitely, unlike the Langmuir case in which the slope of the isotherm must approach zero as saturation is approached. In the BET model, monolayer formation still presumes a heat of adsorption similar to the Langmuir case. But, the rate of adsorption onto the monolayer is presumed to be equal to the rate of desorption from the second layer. A similar argument extends to the third, fourth, and further layers. For adsorption onto the second, third, and subsequent layers, the surface is different. The surface no longer consists of surface atoms of catalyst, but rather consists of atoms of the same substance that has already collected on the catalyst surface. So, for the second, third, and further layers, the process is very much like the condensation of gas to liquid. Therefore, in the BET model the heat of adsorption for the second and subsequent layers is essentially the heat of condensation or vaporization of the gas,  $\Delta H_{vap}$ .

The BET equation is

$$p/n(p_0-p)=1/n_m c,$$

where *n* is molar amount adsorbed at pressure *p*,  $p_0$  is the saturated vapor pressure of the gas at the temperature of the experiment,  $n_m$  is the amount required to cover the surface as a monolayer, and *c* is a constant related to adsorption energy. Generally

$$c = \exp[(\Delta H_{\rm d} - \Delta H_{\rm vap})]/RT$$
,

where the enthalpy terms are for desorption and for vaporization/condensation, respectively.

There are several ways of treating BET data. One form of the BET isotherm equation is

$$V/V_{\rm m} = cZ\{(1-Z)[1-(1-c)Z]\}.$$

Here, V is the volume of gas adsorbed,  $V_{\rm m}$  is the volume expected for monolayer coverage, and Z is the ratio of the actual partial pressure of the gas, p, to the vapor pressure above the pure bulk liquid,  $p_0$ . A BET isotherm could then look like the example shown in Figure 13.9.

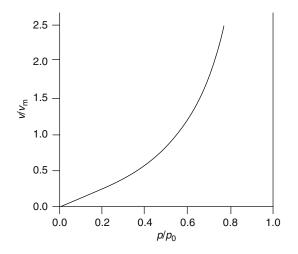


Figure 13.9 An example of a BET adsorption isotherm.

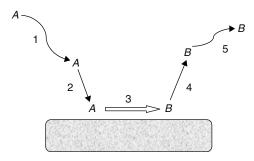
BET data can be used to calculate surface area. Knowing the amount of material adsorbed in a monolayer allows calculation, in straightforward fashion, of the number of atoms or molecules adsorbed. Knowing the size of one atom or molecule allows calculating the surface area. The importance to catalysis lies in the fact that, all other factors being equal, the greater the surface area, the greater the reactivity. Surface area measurements are also important for substances used to adsorb materials, such as activated carbons.

# 13.3 Mechanisms of catalytic reactions

Reactions involving heterogeneous catalysis occur at the interface between a solid catalyst and a fluid phase. Most occur in five steps, see Figure 13.10. First, the reactant diffuses through the fluid to the vicinity of the catalyst. Second, the reactant is adsorbed onto the catalyst surface. Third, the adsorbed species undergoes a reaction on the surface, in which it is converted to the product. Fourth, the product desorbs from the surface. Finally, the desorbed product diffuses away from the catalyst back into the fluid stream. This sequence of steps constitutes the Langmuir–Hinshelwood mechanism of heterogeneous catalysis [D]. Usually, but not always, the third step, conversion of the adsorbed reactant on the catalyst surface, is the rate-determining step in the Langmuir–Hinshelwood mechanism.

The Eley–Rideal mechanism [E] is a process in which a reactant species that has not been adsorbed, i.e. is still in the fluid phase, reacts by colliding with species adsorbed on the catalyst surface, or reacts after first undergoing an extremely weak physical adsorption on the catalyst. A reaction important in fuel chemistry that can proceed via the Eley–Rideal mechanism is that of carbon dioxide in the gas phase with hydrogen adsorbed onto a catalyst,

$$CO_2(g) + H_2(cat) \rightarrow CO + H_2O.$$



**Figure 13.10** The Langmuir–Hinshelwood mechanism, in which (1) a reactant *A* diffuses to the region of the catalyst surface, (2) adsorbs onto the catalyst surface, (3) after which *A* converts to the product *B* on the surface, (4) then *B* desorbs from the surface, and finally (5) *B* diffuses away from the catalyst.

This is important in the water-gas shift reaction (Chapter 20), and may have applications in carbon dioxide capture or destruction processes.

# 13.4 Measures of catalyst performance

When a catalyst is placed in service, it is important to have some quantitative measure of its performance. Several parameters can be used. Activity is defined as the rate of consumption of reactant. For a generic reactant A, the measure of activity would be -d[A]/dt, where t is time. Sometimes more detailed information is useful. Regardless of the reaction being considered, or of the nature of the catalyst, the catalytic activity of any surface depends on an interaction between the reactant and the active sites on the catalyst surface. Active sites are those places on the surface where the catalytic reaction can occur. Not all of the surface is usually active. The exact nature of active sites in many catalytic reactions, and sometimes even how to measure them, remain topics of debate. Especially for supported catalysts, the catalytically active species may not cover the surface uniformly. If the number of active sites per unit volume of catalyst,  $S_V$ , is known, the specific activity per unit volume,  $A_{SV}$ , can be defined as

$$A_{\rm SV} = (-1/S_{\rm V})(\mathrm{d}[A]/\mathrm{d}t).$$

An alternative approach uses the number of catalytically active sites per unit surface area,  $A_{SA}$ :

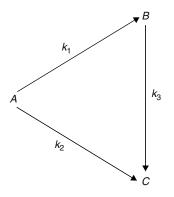
$$A_{\rm SA} = (-1/S_{\rm V})({\rm d}[A]/{\rm d}t).$$

Industrial processing is often limited by the volume of an available reactor, in which case  $A_{SV}$  may provide the more useful measure.

The turnover number, T, expresses catalyst performance in terms of the number of molecules reacted per active site per second. Turnover number can be found from

$$T = A_{\rm SV} N_{\rm A}$$
,

where  $N_A$  is Avogadro's number. In comparing the activities of various catalysts, turnover numbers must be used with caution. If the amount of surface area per unit



**Figure 13.11** The possibilities for reactant *A* converting either to product *B* or to product *C*, and *B* itself also forming *C*. The outcomes of these reactions depend on the relative magnitudes of the rate constants  $k_i$ .

volume of the catalyst is low, then necessarily there are not many active sites per unit volume. Each active site could have a high turnover number, i.e. be reacting furiously, but because few active sites are available, the rate of consumption of reactant is low.

Often, especially in organic reactions, a reaction could lead to several different products (isomers, for example) or there could be several competing reactions. The concept of selectivity provides a second important measure of catalyst performance. Catalyst selectivity is defined as the fraction – either as mole fraction or weight fraction – of the desired product(s) in the total moles, or total mass, of all products.

Catalysts are characterized by both activity and selectivity. Activity and selectivity are *not* synonymous. Four combinations are possible: a catalyst with high activity and high selectivity represents the ideal. High activity but low selectivity could be acceptable provided that separation of co-products is relatively easy (a carboxylic acid from an alkane, for example) and that each of the co-products has some value. The reverse, a catalyst of low activity but high selectivity, may be acceptable if the desired product is of high value, if the downstream separation of co-products would be difficult, or if the unconverted feed could be recycled back through the reactor. The final possibility, a catalyst of low activity and low selectivity, simply leads to the conclusion that it is time to pick a different catalyst.

Sometimes, the *un*desired product is the thermodynamically stable one. Thus it is necessary to try to outwit thermodynamics, and the only weapon available to do that is kinetics. As an example, there might be three generic reactions: the desired  $A \rightarrow B$ , but where another reaction,  $A \rightarrow C$  is possible, as is a third reaction  $B \rightarrow C$ . Each reaction has a rate constant, say,  $k_1$ ,  $k_2$ , and  $k_3$ , respectively. If  $k_2$  and  $k_3$  are small relative to  $k_1$ , then it is often possible to design a catalyst that gives high selectivity. If only  $k_3$  is small, then selectivity is constant as a function of conversion. Selectivity is generally related to the ratio of the rate constants. If  $k_3$  is not small, as the reaction proceeds, sooner or later everything will convert to *C*. If the reaction is run to total conversion, what would be observed in this case is shown in Figure 13.11.

The only other strategy should be evident from the shape of this line – the reaction must deliberately be run at low conversion, to stay in the region where selectivity is acceptable.

**Figure 13.12** Sintering of catalytically active surface species (here depicted with circles) involves their migration to a point of touching, and then a partial melting that creates one new particle from the original two. The effect is to reduce the surface area of the active species, and thus to reduce the activity of the catalyst.

## 13.5 Surface effects on catalysts

Obtaining a catalyst suitable for a particular process involves selecting the catalytic material that is active for the desired reaction, usually selecting a support that gives satisfactory performance, and producing the material so that it has acceptable activity and selectivity. But it also becomes necessary to take into consideration processes that would deactivate the catalyst, i.e. reduce or even destroy its activity. Processes that harm the catalyst surface, or hinder access to active sites, reduce the activity of the catalyst. In extreme cases, such processes completely destroy the activity of the catalyst. Three such processes are of concern.

If the temperature of the catalyst gets too high, particles of the active catalyst may partially melt and fuse together, a process known as sintering. This process reduces the total surface area of the active catalyst (Figure 13.12), causing a drop in catalyst activity.

The onset of sintering depends on a number of factors. As a rule, sintering can be expected when the temperature of the material reaches one-half of its melting point in kelvin. For example, the melting point of nickel is  $1455 \,^{\circ}$ C, or  $1728 \,$ K. Sintering may become important at  $\approx 864 \,$ K, or  $590 \,^{\circ}$ C. Sintering is irreversible. There is no way to "unsinter" a catalyst, short of grinding it up, separating the catalytic material from the support, and reprocessing the catalytic material somehow to produce a new batch of catalyst.

Sintering occurs at high temperatures, one of the driving forces being the ability to reduce surface area and, consequently, surface energy. For metals and metal oxides, the primary mechanism is bulk diffusion in the solid state. When this happens, there are two effects. First, even if the particles sintered together while just touching, there would be some reduction in surface area. However, the sintering via bulk diffusion also results in a net shrinkage in volume. Thus an even greater reduction in total surface area, and hence reduction in surface energy, occurs. When sintering occurs, the reaction rate decreases.

The role of temperature for sintering derives from the fact that diffusion is an activated process, with a characteristic activation energy. The diffusion coefficient indicates the speed with which atoms or ions can move through the solid. At high temperatures, the diffusion coefficient has a strong temperature dependence (high activation energy). A relatively small increase in temperature can cause a significant increase in diffusion coefficient.

In the case of catalyst poisoning, some substance in the feed reacts with the catalytically active species to form a new compound on the surface, but one of lower activity than the original catalyst, or possibly one with no catalytic activity at all. Poisons can be considered to be the opposite of promoters, in the sense that poisons are substances that decrease one or more of the desirable properties of a catalyst. Catalyst poisons tend to be electronegative elements or their compounds, such as compounds containing sulfur or nitrogen.

Sulfur or its compounds often act as catalyst poisons. For example, sulfur reacts with nickel or platinum to form sulfides that have little or no catalytic activity. As sulfur compounds build up on metal surfaces, they block access of reactive species to the catalyst surface. The nickel catalyst used for methane synthesis (Chapter 21) can be poisoned by hydrogen sulfide, even at very low concentrations.  $H_2S$  undergoes dissociative chemisorption on the catalyst surface, and the relatively large sulfur atom – the radius of S<sup>-2</sup> is 184 pm, compared with 69 pm for Ni<sup>+2</sup> – blocks several adjacent active sites. A surface electronic effect in this case works oppositely to that of the promoter, reducing the electronic interaction of incoming molecules with the catalyst, and making them less likely to undergo dissociative chemisorption. Some catalysts have active sites that are Lewis acids, i.e. electron-pair acceptors. Nitrogen compounds with an unshared pair of electrons with the surface.

Several approaches can be taken to ward off poisoning. The feed can be carefully cleaned (e.g. acid gas removal processes, Chapter 20) before entering the catalytic reactor. A "guard bed" of some inexpensive and expendable material can be used upstream of the catalytic reactor to remove sulfur compounds before they encounter the catalyst. Zinc oxide is an example:

$$ZnO + H_2S \rightarrow ZnS + H_2O.$$

The catalyst could be changed to one that is more tolerant of sulfur. Indeed, some metal sulfides, such as  $MoS_2$ , are themselves good catalysts. In favorable cases, poisoning can be reversed. Careful heating at high temperatures but very low pressures might entice the poison to desorb. Sometimes it may be possible to remove the catalyst by chemical reaction, e.g.

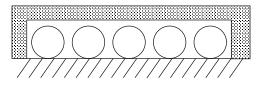
$$PtS_2 + 2H_2 \rightarrow Pt + H_2S.$$

If the surface interaction with sulfur or nitrogen compounds is weak, raising the temperature and reducing the pressure might cause some of these compounds to desorb from the surface.

Catalyst poisons function in various ways. The most direct is simple blocking of the active sites on the catalyst. Formation of coke on the catalyst surface provides an example. Coke deposition, or catalyst coking, puts a layer of carbon on the catalyst surface, blocking access to the active sites. The process involves formation of a carbon-aceous surface layer on the catalyst surface during various reactions of hydrocarbons. When the catalyst surface is coked, reactant molecules no longer have access to the active sites. The reaction stops, and the activity of the catalyst is essentially gone.

Coking on a catalyst surface is analogous to the hydrogen redistribution processes discussed in Chapters 7 and 8. Coking is particularly likely in reactions involving internal transfer of hydrogen, because of the inevitable formation of carbon-rich products, as shown in Figure 13.13.

The products are a carbon-rich, highly aromatic solid and hydrogen-rich, low molecular weight hydrocarbons. Aromatic carbocations are quite stable relative to aliphatic carbocations, because the charge can be delocalized over the aromatic system, rather than localized on one carbon atom. Aromatic carbocations can remain on the catalyst surface and grow to very large molecular structures. Hydrogen redistributed from the coking reactions helps to convert alkenes to alkanes. The rate of coke



**Figure 13.13** Catalyst coking involves partial or complete covering of the catalytically active surface species (here again depicted with circles) by a layer of carbonaceous coke. The effect is to block reactant access to the active species, making them no longer available for reaction. Again the activity of the catalyst is reduced.

formation from various precursors decreases in the order naphthalene derivatives > benzene derivatives > alkenes > cycloalkanes > alkanes. Process streams rich in aromatics produce cokes that are highly aromatic, nearly graphitic in structure. Alkanes and alkenes tend to produce less aromatic, more amorphous cokes. Coke can plug pores or occlude the surface, reducing or destroying catalyst activity and requiring that the catalyst surface be regenerated.

Coking is increased if the catalyst surface is too acidic, and is enhanced by increased temperature. Thus careful control of the catalyst surface properties (in this example, surface acidity), and reaction conditions can be helpful in avoiding or reducing coking. Of the three "catalyst killers," sintering, poisoning, and coking, coke is the easiest to deal with. A *careful* exposure of the coked catalyst to oxygen or air can burn off the coke and restore the activity of the catalyst. Since coke burn-off is exothermic, caution is needed to avoid sintering the catalyst at the same time. This process of catalyst regeneration also has the potential pitfalls of inadvertently altering the pore size distribution in the support, or possibly losing some of the catalyst via formation of volatile oxides. This last process can happen, for example, with platinum–iridium alloys, where volatile iridium(VI) oxide, IrO<sub>3</sub>, can form and be lost.

#### Notes

- [A] Though homogeneous gas-phase catalysis is rare, a very important example is the depletion of stratospheric ozone by chlorofluorocarbons (CFCs). CFCs are decomposed by ultraviolet light, yielding chlorine atoms, Cl•, as one product. These atoms react with ozone to form chlorine oxide and oxygen, Cl• + O<sub>3</sub> → ClO +O<sub>2</sub>. Chlorine oxide also reacts with ozone, regenerating the chlorine atom: ClO + O<sub>3</sub> → Cl• + 2O<sub>2</sub>. Ozone depletion, particularly in the southern hemisphere, is of concern as a potential skin-cancer risk, because people would be exposed to greater levels of incident ultraviolet light.
- [B] Irving Langmuir (1881–1957, Nobel Prize 1932) spent most of his career in the research laboratories of General Electric. His numerous contributions to the fundamental understanding of surface phenomena led to garnering many prestigious awards, both in the United States and abroad. His fundamental studies led to, among other practical inventions, the gasified incandescent lamp (prior to Langmuir's work, bulbs were evacuated to prevent the filament from reacting or

burning), and the atomic hydrogen welding process. The journal devoted to surface phenomena published by the American Chemical Society is fittingly called *Langmuir*.

- [C] Stephen Brunauer (1903–1986), a Hungarian immigrant to the United States, spent much of his career as a civilian chemist working for the United States Navy, in the explosives division. Perhaps his most remarkable accomplishment, aside from the BET model, was his hiring of Albert Einstein as a consultant at a salary of \$25 per day. Brunauer was one of the numerous targets of the extreme-right hysteria touched off by Senator Joseph McCarthy. Later in his career he worked for the Portland Cement Association. Paul Emmett (1900-1985) was educated in Oregon, where he was a classmate, friend, and eventually brother-in-law of Linus Pauling. Emmett spent much of his career at Johns Hopkins University. His work with the Manhattan Project during World War II led to development of a process of uranium enrichment. Edward Teller (1908-2003), another Hungarian immigrant, is probably best known nowadays as the "father of the hydrogen bomb." He is also famous, or notorious, for being the inspiration for the character Dr. Strangelove, in the movie of the same name. Late in his career, Teller was an enthusiastic backer of President Reagan's Strategic Defense Initiative ("Star Wars") and advocated such schemes as dredging a new harbor in Alaska by setting off thermonuclear explosions.
- [D] Sir Cyril Hinshelwood (1897–1967, Nobel Prize 1956) was an English physical chemist who spent most of his career at Oxford. His extensive studies of molecular kinetics included pioneering work on chemical changes in bacterial cells, which inspired subsequent research in antibiotics.
- [E] Sir Eric Rideal (1890–1974), like many of the other personalities mentioned in these notes, had a multifaceted career. He made contributions to electrochemistry, water treatment and purification, and surface chemistry. Rideal wrote numerous monographs and textbooks, including noteworthy books on catalysis in 1919 and on surface chemistry in 1926. Much of his career was spent as a lecturer in colloid science at Cambridge University.

#### Recommended reading

- Bowker, Michael. *The Basis and Applications of Heterogeneous Catalysis*. Oxford University Press: Oxford, 1998. This short monograph on heterogeneous catalysis provides a very useful introduction to the essential principles of the field.
- Bruch, L.W., Cole, Milton W., and Zaremba, Eugene. *Physical Adsorption*. Dover Publications: Mineola, NY, 1997. A detailed discussion of the physics of adsorption of gases on surfaces, with extensive theoretical discussions.
- Gates, Bruce C. *Catalytic Chemistry*. Wiley: New York, 1992. An excellent textbook intended to cover most of the field of catalysis, by a world-class expert in the field. Chapter 6 relates particularly to the present chapter.
- Kolasinski, Kurt W. *Surface Science*. Wiley: Chichester, 2008. This book provides a detailed discussion of dynamics of adsorption and desorption, surface structures, and catalysis. Chapter 6 is particularly relevant to the present chapter.
- Le Page, J.F. *Applied Heterogeneous Catalysis*. Éditions Technip: Paris, 1987. Detailed treatment of using catalysts, beginning with selection, through preparation and properties measurement, to designing catalytic reactors.

- Rothenberg, Gadi. *Catalysis: Concepts and Green Applications*. Wiley-VCH: Weinheim, 2008. A useful monograph that covers both homogeneous and heterogeneous catalysis. Chapters 2 and 4 are specifically relevant here.
- Vannice, M. Albert. *Kinetics of Catalytic Reactions*. Springer: New York, 2005. As the title implies, the principal focus is on acquiring reaction rate data, kinetic analysis, and modeling reactions on surfaces.

Gasoline, or petrol, consists almost entirely of low-boiling hydrocarbon molecules, with very small amounts of NSOs. Gasoline used world-wide amounts to  $\approx 2.5$  megatonnes per *day*, about half being consumed by the United States. Virtually all comes from petroleum. A small amount, on a world basis, is made in South Africa from coal, by the process of indirect liquefaction (Chapter 21).

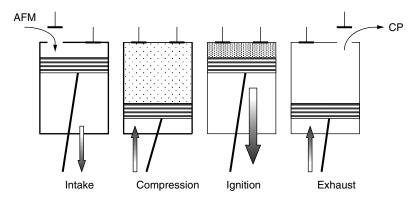
Production of any petroleum product begins with distillation. Petroleum is distilled into fractions (or "cuts") characterized by a particular boiling-point range. A single distillation cut has components of sufficiently similar properties so that the entire fraction is of reasonably consistent quality. The first liquid to come off the distillation column is gasoline [A]. Its boiling range is from the initial boiling point to 180 °C. That is, whether a petroleum product is or is not gasoline is determined by its boiling range, which, in turn, is determined largely by molecular size. Compounds in gasoline range up to about  $C_{12}$  in size, and consist of straight- and branched-chain alkanes, single-ring cycloalkanes and their alkylated derivatives, and benzene and alkylbenzenes.

# 14.1 Gasoline combustion

The property of gasoline having major importance is its performance as a fuel for spark-ignition internal combustion engines. By far the dominant use of gasoline is as fuel for automobiles and light trucks, and the dominant engine in these vehicles operates on the four-stroke cycle (Figure 14.1) developed by Nikolaus Otto (Figure 14.2) about 125 years ago [B].

In the intake, or induction, stroke, the piston travels downward, and a fuel-air mixture is drawn or injected into the cylinder. In the second stroke, compression, the piston moves upward and, as the name implies, compresses the fuel-air mixture in the cylinder. In the third stroke, called the ignition, working, or power stroke, an electric spark ignites the compressed fuel-air mixture. As the mixture burns, temperature and pressure inside the cylinder rise. Increased pressure pushes the piston downward. This stroke converts the chemical energy in the gasoline molecules into the mechanical work that propels the vehicle. The piston comes back up in the exhaust stroke, sweeping the products of combustion out of the cylinder.

At the instant of ignition, only a tiny portion of the air-fuel mixture in the immediate vicinity of the spark plug tip ignites. The ignition produces a flame, roughly hemispherical, that progresses as a wave through the air-fuel mixture. The entire combustion of the air-fuel mixture takes a few tens of milliseconds, but even so, in a well-tuned engine there is no instant when any more than a small fraction of the fuel is burning at a time.

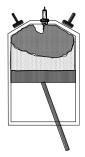


**Figure 14.1** The four-stroke Otto cycle. In the intake stroke, the piston is pulled down by the engine crankshaft and an air-fuel mixture (*AFM*) is drawn into the cylinder. The mixture is compressed during the compression stroke, as the piston is pushed upward. In the ignition stroke, the mixture is ignited by an electric spark; the chemical energy in the gasoline is converted to mechanical work that pushes the piston down. In the exhaust stroke, the crankshaft pushes the piston up and sweeps the combustion products (*CP*) out of the cylinder.



**Figure 14.2** Nikolaus Otto, inventor of the four-stroke-cycle gasoline-fueled internal combustion engine.

This ensures that the chemical energy of the fuel is released smoothly and uniformly, not violently. Figure 14.3 provides a conceptual snapshot of a point part-way through the combustion process. Here, the temperature and pressure of the unburned portion of the fuel are steadily rising. Depending on fuel composition and the specific combustion conditions, a temperature/pressure combination can be attained at which the remaining fuel undergoes autoignition. Autoignition, sometimes called self-ignition or spontaneous combustion, occurs when the composition, temperature, and pressure of the fuel–air system enter the explosion regime. With a liquid fuel such as gasoline, the fuel attains the vapor pressure corresponding to its value at the temperature of the hot combustion gases. When this happens, all of the unburned fuel–air mixture burns essentially instantaneously, rather than burning out smoothly as the flame propagates through the mixture. Autoignition is a miniature explosion so severe that it can be heard by the driver, and, for this reason, is commonly called engine knock.



**Figure 14.3** Combustion begins with ignition of the fuel-air mixture by the spark plug. Part-way through the combustion process some of the mixture has burned, but there is still unburned fuel-air mixture (indicated by the lightly dotted area) in the cylinder. The temperature and pressure of this as-yet-unburned mixture are increasing.

Engine knock presents several problems. First, since the fuel does not burn out smoothly, efficiency is lost. The driver sees this as reduced fuel efficiency, as more liters per kilometer or fewer miles per gallon. Chronic engine knock wastes fuel. Second, because the engine does not operate at optimum efficiency, performance also suffers, as, e.g., in reduced acceleration. Third, engine knock puts mechanical stresses on engine parts such as piston rods and cylinder heads. On an equal mass basis, a gasoline–air mixture is a more violent and devastating explosive than dynamite. Chronic, uncorrected engine knock can lead to major maintenance problems well before they might reasonably have been expected in a well-tuned engine.

The first high-performance, eight-cylinder came on the market in the early 1930s. Efforts to improve the performance of engines, especially power, continued through the 1930s and beyond. Three factors determine the power rating of an engine: effective average pressure in the cylinders during the operating cycle, total swept volume (i.e. volume displaced by all the pistons moving through the full length of the stroke), and average piston speed. Increasing the effective average pressure increases thermal efficiency. More of the chemical energy in the fuel is converted to useful mechanical work in the engine.

The volume of an engine cylinder can be expressed in two ways: either volume when the piston is at the top of its stroke, or when it is at the very bottom. These two volume measurements can be labeled arbitrarily as  $V_1$  and  $V_2$ , respectively. Their ratio, specifically  $V_2/V_1$ , defines a characteristic parameter of an engine, its compression ratio. The higher the compression ratio, the more the fuel-air mixture is compressed during compression, making the pressure inside the cylinder higher at the moment of ignition. In engines used nowadays in automobiles and light trucks, the compression ratio is usually in the range of 8:1 to 10:1, though a few high-performance engines equipped with knock sensors have had compression ratios as high as 13:1. The pressure is already higher, even before combustion begins, in the cylinder than would be the case for an engine of lower compression ratio. So, the chances that, during combustion, pressure will build to a point of knocking are also greater. The higher the compression ratio of an engine, the more likely is the engine to knock, when running on a given fuel. As engine performance steadily increased with the continual development of higher compression engines after the 1930s, there came a need for gasolines with less tendency to knock.

On a molecular level, combustion proceeds via radical processes involving reactions of hydrocarbon molecules with oxygen. These reactions were introduced in Chapter 7.

The approach taken to understand the relationships between engine performance, fuel composition, and engine knock was to study the combustion behavior of a variety of pure compounds typical of the components of gasoline. The study showed that branched-chain alkanes are less likely to knock than are straight-chain compounds, in similar engines operated under comparable load. A key initiation reaction is that of molecular oxygen with a fuel molecule, e.g.

$$RH + O_2 \rightarrow R \bullet + \bullet O_2 H.$$

For this bimolecular reaction to occur, the two molecules interact via London-force attractions. One factor in explaining the behavior of branched-chain molecules is their smaller surface area relative to the straight-chain isomers. This distinction may result in a slightly reduced likelihood of the bimolecular initiation reaction. In combustion of a straight-chain alkane the reaction

$$\mathbf{R} \bullet + \mathbf{O}_2 \to \mathbf{ROO} \bullet$$

is likely to involve a 1° radical, but radicals from branched-chain molecules can be the more stable 3° radicals. For radicals such as •OH or •O<sub>2</sub>H interacting with a C–H bond, activation energy decreases in the order  $1^{\circ} > 2^{\circ} > 3^{\circ}$  for the hydrocarbon radical produced by hydrogen abstraction. For example, reactions with the •OH radical have activation energies of 28 kJ/mol for a 1° C–H bond, 23 kJ/mol for 2°, and 20 kJ/mol for 3°. The reduced London-force interactions and the greater stability of 3° radicals reduce the likelihood of autoignition.

To obtain a quantitative comparison of knocking behavior, two compounds were selected as reference points. Heptane, a linear alkane, was arbitrarily assigned a value of 0, and the highly branched 2,2,4-trimethylpentane was assigned a value of 100. 2,2,4-Trimethylpentane has eight carbon atoms, so is often, but quite incorrectly, called "isooctane," (isooctane is 2-methylheptane) and occasionally even worse, "octane." Nonetheless, this misuse of organic nomenclature persists, and the numerical datum used to express gasoline combustion performance is known as the octane number. The octane numbers of a variety of pure hydrocarbons are given in Table 14.1.

Octane number of *n*-alkanes decreases with increasing number of carbon atoms. Octane number increases as chain branching increases. Cycloalkanes have higher octane numbers than alkanes, and aromatics have still-higher octane numbers. Improvements in octane rating can be obtained by converting longer alkanes to shorter ones, by increasing chain branching, and by forming cycloalkanes and aromatics [C].

The octane number of any given gasoline is equal to the percentage of 2,2,4trimethylpentane in a test blend of 2,2,4-trimethylpentane and heptane that gives the same performance as the gasoline being tested. Several measures of octane number are used. Research octane number (RON) indicates fuel performance under relatively lowseverity operation. Measurement is done in a carefully controlled single-cylinder engine of variable compression ratio, running at 600 rpm. Motor octane number (MON) is obtained in a similar test engine but operating at 900 rpm to be more indicative of highload or high-speed driving conditions. For many pure compounds and actual fuels, MON is the lower number, often by some eight to ten points. The difference between RON and MON has led some countries, including the United States, to adopt an anti-

Compound	Research octane number	Compound	Research octane number
C <sub>4</sub> compounds		C <sub>7</sub> compounds, cont'd.	
<i>n</i> -Butane	93	Methylcyclohexane	75
C <sub>5</sub> compounds		2,2-Dimethylpentane	93
<i>n</i> -Pentane	62	2,2,3-Trimethylbutane	113
1-Pentene	91	Toluene	124
2-Methyl-2-butene	97	$C_8$ compounds	
2-Methylbutane	99	2-Methylheptane	23
2,2-Dimethylpropane	100	Ethylcyclohexane	43
Cyclopentane	101	1.3-Dimethylcyclohexane	67
$C_6$ compounds		1,4-Dimethylcyclohexane	68
<i>n</i> -Hexane	25	2,3-Dimethylhexane	71
2-Methylpentane	73	1,2-Dimethylcyclohexane	81
3-Methyl-2-pentene	78	2,2,4-Trimethylpentane	100
Cyclohexane	83	2,2,4-Trimethyl-2-pentene	113
Methylcyclopentane	91	o-Xylene	120
2,2-Dimethylbutane	92	Ethylbenzene	124
2,3-Dimethylbutane	92	2,4,4-Trimethyl-1-pentene	125
4-Methyl-2-pentene	99	<i>m</i> -Xylene	145
Benzene	106	<i>p</i> -Xylene	146
C <sub>7</sub> compounds		C <sub>9</sub> compounds	
<i>n</i> -Heptane	0	Propylbenzene	127
2-Methylhexane	44	Isopropylbenzene	132
1-Heptene	60	1,3,5-Trimethylbenzene	171

 Table 14.1
 Research octane numbers of selected hydrocarbons.

knock index (AKI), also called the pump octane number or the road octane number, which is the average of the RON and MON. Usually the AKI is the number posted on gasoline dispensing pumps as the octane rating. Yet another octane number comes from the fact that often the octane number of a blend of compounds is not a simple linear combination of the RONs of the pure compounds. A blending octane number (BON) is determined by mixing 20% of the compound of interest with 80% of a 60:40 blend of 2,2,4-trimethylpentane and *n*-heptane. Some compounds display very large differences; as an example, 2-methyl-2-butene has a RON of 97, but a BON of 176.

Three general rules-of-thumb can be established: when using a given gasoline, the higher the compression ratio, the greater the likelihood of engine knock. In a given engine, the higher the octane number of the fuel, the less is the tendency to knock. Engines of high compression ratio normally require gasolines of higher octane rating to avoid knocking [D].

The continuing need for increasing octane number is illustrated by trends in engine design and performance. In the 1920s, a typical automobile engine had a compression ratio of about  $4\frac{1}{2}$ :1. It would run well on 55-octane gasoline, and generated about 10 kilowatts per liter of cylinder volume. Forty years later, the high-performance engines in the "muscle cars" of the 1960s had compression ratios of  $9\frac{1}{2}$ :1, producing 36 kW/l. These engines required gasoline of  $\approx$ 93 octane. Nowadays the highest rating for a four-cylinder engine (in the Honda S2000) is nearly 90 kW/l, with a compression ratio of 11:1. This vehicle uses 91-octane (AKI) gasoline. Most modern gasoline-fueled vehicles have compression ratios in the range 8:1 to 10:1, with octane requirements of 87–93.

# 14.2 Specifications and properties of gasoline

Many countries set specifications for gasolines that go well beyond boiling range and octane number. Indeed, even many states, regions, or municipalities set specifications for gasolines. This plethora of specifications does not make life easy for refiners, where individual refineries may produce thousands to tens of thousands of tonnes of gasoline per day. The term "boutique fuel" is sometimes used – often disparagingly – to refer to a gasoline that must be formulated and produced in relatively small quantity to meet unique specifications set by some local or regional authority. In addition to the formal specifications, several additional properties have important roles in gasoline performance, though consumers and regulators seldom pay attention to them. The discussion that follows refers to numerical values that may be *typical* of gasolines, but it should be understood that actual values can vary from place to place.

A common approach to specifying distillation behavior is to indicate temperatures at which a particular volume of gasoline should have been distilled. For example, 50% of the gasoline should have distilled by 100 °C, and 90% by 150 °C. In the latter example, a specification might refer to "90% over" with a temperature value of 150 °C.

Many aromatic compounds have very high octane numbers (Table 14.1). From that perspective, they should be desirable components of gasolines. However, aromatics have two negative factors. First, many aromatic compounds are suspect or proven carcinogens. Potentially, chronic exposure to aromatic compounds, via inhalation of gasoline vapors or transmission through the skin from contact with liquid gasoline, might lead to cancer. Second, aromatic compounds are precursors of soot formation during combustion. (This is more of a problem with middle distillate fuels discussed in Chapter 15.) For these reasons, the content of aromatic compounds in gasoline is specified commonly to a maximum limit of 25% by volume. Benzene in particular is of concern, nowadays listed as a known carcinogen, with chronic exposure possibly leading to leukemia. Many gasoline specifications therefore put an additional limit on allowable benzene content, usually less than 1% by volume.

Alkenes – usually referred to as olefins – also have high octane numbers. Partial oxidation and subsequent oligomerization of alkenes produces high-viscosity, high-molecular-weight materials called gums. They can foul the intake manifold, block fuel pump membranes, nozzles, and fuel injectors, and in extreme cases can cause sticking of piston rings. Gum formation probably begins with the interaction of gasoline components with dissolved oxygen to form peroxy or hydroperoxy radicals. These radicals then begin a series of propagation reactions that lead to larger and larger molecules. The high-molecular-weight compounds formed through such processes eventually form a separate phase. Alkene content in gasolines is usually limited to ten percent or less.

Hydrocarbon molecules in gasoline are not corrosive toward metals. Gasoline can contain traces of substances, such as sulfur compounds, organic acids, and water, that could eventually cause corrosion of metal parts in fuel lines and in the engine. Of these, carboxylic acids are the most acidic, and potentially the most corrosive. Total oxygen content is usually limited to being less than 0.1%. (However, if the gasoline contains ethanol or other oxygenated compounds deliberately added as blending agents, they are not counted against the total oxygen content specification.)

Vapor pressure affects gasoline performance in several ways. Gasoline must vaporize readily upon injection into the cylinder. On a very cold winter day, we still expect the

engine to fire as soon as the starter begins to turn the engine. This requires a fuel of very high vapor pressure, so that even at temperatures well below 0 °C enough of the fuel will evaporate to ignite. This behavior is sometimes called cold-start performance. At the other extreme, on a very hot summer day a fuel of high vapor pressure could evaporate in the fuel line even before it gets to the engine. This problem, sometimes called vapor lock, causes the engine to shut down until it becomes cool enough for the fuel to condense. Ideally, for winter driving one wants a gasoline with good cold-start performance, but in summertime one wants to avoid vapor lock. Refiners do a good job of meeting these concerns by shifting the distillation cut points slightly to adjust the vapor pressure of gasoline with changing seasons.

Vapor pressure also affects evaporation of gasoline, which contributes to air pollution. In the presence of sunlight, gasoline vapor interacts with carbon monoxide and nitrogen oxides, by-products of gasoline combustion, to create the air-pollution problem known as photochemical smog, or just "smog" [E]. Some of the unburned gasoline comes from material that swept through the engine without burning, but some also comes from gasoline that evaporates from fuel tanks, fuel lines, and spills. The higher the vapor pressure, the higher the tendency to evaporate, hence the greater contribution of gasoline vapors to the air.

A commonly used approach to vapor pressure specifications for gasoline is the Reid vapor pressure (RVP). It is the absolute vapor pressure of the liquid measured at  $37.8 \,^{\circ}$ C. RVP specifications vary from one region to another and often vary with season of the year as well. Representative RVP values for gasolines would be in the range  $40-50 \,$  kPa.

Normally, gasoline has a very low sulfur specification, often in the range 15–30 ppm. Sulfur content is of concern in part because sulfur in fuel is converted to sulfur dioxide and trioxide during combustion. If these sulfur oxides are allowed to escape into the environment, they contribute to the pollution problem known usually as acid rain. In addition, some sulfur compounds are mildly acidic and could contribute to corrosion. The more reactive sulfur functional groups – thiols, aliphatic sulfides, and disulfides – can also have a role in gum formation. Thus numerous reasons support very low sulfur specifications for gasolines.

Density was once used as a criterion of gasoline quality, but is no longer an important specification. Generally, aromatics and sulfur compounds have noticeably higher density than alkanes. Unusually high density in gasoline might signal a product that has a high concentration of one or both of these undesirable components. Gasolines generally have densities from  $0.70 \text{ g/cm}^3$  to about  $0.77 \text{ g/cm}^3$  (52–71° API). Volumetric energy density is the heat of combustion per unit volume, i.e. MJ/l. Its importance derives from the fact that gasoline purchase is made by volume, not by weight. For most vehicles, the limit to how much fuel can be carried is the volume of the fuel tank, and not fuel weight. Volumetric energy density varies over a narrow range for gasoline, and typically is about 45 MJ/l.

Under most circumstances, the viscosity of gasoline is so low – typically 0.5 mPa $\cdot$ s at 15 °C, half the value of water at the same temperature – that it is not of concern in gasoline performance. The viscosity of all liquids increases as temperature decreases, but the viscosity of gasoline would never get high enough to cause problems.

The flash point of a liquid fuel is the temperature at which sufficient vapor exists above the liquid to sustain a flame - in other words, the temperature at which the

vapors will ignite when exposed to an ignition source. Flash point data, even for the same sample, vary depending on whether the liquid was heated in a closed or open container, and the distance of the ignition source (i.e. a flame) above the liquid. These parameters are controlled for any particular variation of the flash point test, but different tests can give somewhat different results. The flash point for gasoline is -40 °C or lower. The advantage of so low a value is that gasoline vapors should be able to "fire" an engine at the lowest temperatures at which anyone is likely to drive. The disadvantage is that gasoline stored where its vapors can accumulate – such as a can of gasoline for lawn-care or snow-removal devices, kept in a closed garage – represents a potential hazard for accidental fires.

Many components of fuel systems, such as hoses, gaskets, and seals, are made of polymers. Gasoline is a reasonably good solvent for some organic materials, and can cause others to swell, so compatibility of fuel system parts with gasoline must be achieved. Normally this compatibility is determined by the manufacturers and never comes up as an issue for the driver. In switching to a fuel with very different formulation, however, problems could arise. The introduction of gasoline–ethanol blends in response to the oil embargo and price shocks of the 1970s caused problems in some vehicles at that time, because the dissolution and swelling behavior of the blends differed from that of gasoline itself.

Aside from the task of meeting the many requirements for chemical and physical properties of gasoline, a second major issue that must be addressed in gasoline production is the larger consumer demand for gasoline. Though many parts of the world show a steady evolution of "dieselization" of the vehicle fleet, other places, especially the United States, continue to rely heavily on gasoline-fueled engines for automobiles and light trucks. In the U.S. the number of registered vehicles now exceeds the number of licensed drivers. The consumer demand for gasoline is approximately equivalent to a 50% yield from crude oil, i.e. conversion of 100 barrels of petroleum to 50 barrels of gasoline, and with octane ratings in the range 87–93. Taking the best case, refining of Pennsylvania-crude quality petroleum would yield, upon distillation, about a 20% yield of 50-octane straight-run gasoline. This mismatch between consumer demand and gasoline quality on the one hand, and what could be obtained by simple distillation of Pennsylvania crude on the other, creates major challenges in petroleum refining.

# 14.3 Refinery routes to enhanced yield and quality

Boiling range is determined by the kinds of hydrocarbon molecule – alkanes, cycloalkanes, or aromatics – present and their size, i.e. the number of carbon atoms in the molecule. Most gasolines are dominated by constituents in the range  $C_5$  to about  $C_{12}$ . Combustion performance of the gasoline, as measured by octane number, also depends on the kinds of molecule, and also on their shape. Branched-chain structures have significantly higher octane numbers than their straight-chain isomers.

To enhance the yield of gasoline, two options are available: first, take molecules smaller than  $C_5$  and put them together to build up molecules in the  $C_5$ - $C_{12}$  range. Examples of this strategy are the alkylation and polymerization processes discussed in the two sections that follow. Second, refineries take products dominated by molecules too large to be in the gasoline boiling range, and break them down, i.e. crack them, into

the  $C_5-C_{12}$  range. Branched-chain alkanes are not common in most oils, so their presence in high-octane gasoline requires that they be produced during these reactions. While most thermal processes involve radicals as intermediates, which normally do not undergo rearrangement of the carbon chain, carbocations can undergo rearrangements. Thus the reaction mechanism for cracking needs to be changed from radical processes to those involving carbocations. A change in reaction mechanism can often be effected by using an appropriate catalyst, which also offers the advantage of enhancing reaction rates. Thus cracking to enhance yield and quality of gasoline should be done in the presence of a catalyst; the term catalytic cracking helps distinguish this approach from thermally driven free-radical processes.

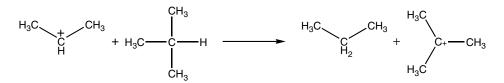
Running alkylation, polymerization, or catalytic cracking processes with carbocation intermediates facilitates formation of branched-chain compounds that enhance octane number while at the same time increasing yield. Another strategy that focuses on improving gasoline quality starts with feedstocks that already boil in, or near, the gasoline range, and rearranges structures to the desired branched-chain, high-octane compounds. Such a process has little effect on yield, but a dramatic one on quality. This re-shaping, or re-forming, of molecules to increase octane number is called catalytic reforming. Catalytic reforming is also a carbocation process.

# 14.4 Alkylation and polymerization

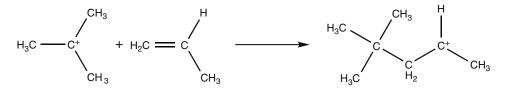
Alkylation and polymerization differ in the nature of the feedstock: polymerization is a reaction between alkenes, whereas in alkylation an alkane reacts with an alkene. The  $C_4^-$  alkenes have valuable uses in the chemical industry [F], but refiners can also use them to enhance the yield of gasoline. The reaction of propylene with 2-methylpropane (isobutane) provides an example. The feedstocks derive from catalytic cracking described below, or from thermal processes discussed in Chapter 16. Propylene can be protonated by a strong Brønsted acid:

$$CH_3CH = CH_2 + H^+ \rightarrow CH_3CH^+CH_3.$$

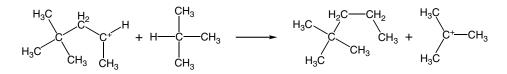
The resulting 2° carbocation readily reacts with the 3° hydrogen atom of isobutane:



The opportunity to form the more stable  $3^{\circ}$  carbocation at the expense of the  $2^{\circ}$  ion drives this reaction. The reactive intermediate is the  $3^{\circ}$  carbocation; propane is a by-product. The electrophilic  $3^{\circ}$  carbocation reacts with the double bond in propylene:



The new  $2^{\circ}$  carbocation formed in this reaction reacts with another molecule of isobutane:

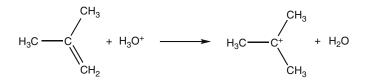


The newly formed carbocation allows the reaction to propagate. The stable reaction product is 2,2-dimethylpentane (neoheptane), a high-octane constituent of gasoline.

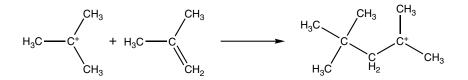
Alkenes in the feed are in the  $C_3$ - $C_5$  range. Reaction temperature is 0–40 °C. Pressure is kept high enough to maintain the reactants in the liquid phase, in the range 0.1–8.5 MPa. In the reaction of isobutane with propylene, the product is a mixture of 60–80% 2,2-dimethylpentane, 10–30% 2-methylhexane (isoheptane), and 10% 2,2,3-trimethylbutane (triptane). The product, called motor fuel alkylate, has octane numbers in the range 90–115. Sulfuric acid has largely replaced hydrofluoric acid as the current choice as an alkylation catalyst, HF being much less safe to handle.

Polymerization combines two small alkene molecules to make a larger molecule in the gasoline range. The term "polymerization" is a misnomer, because what is really happening is a dimerization. True polymerization is certainly possible with the small alkenes used in this process. For example, at 100 °C, a solution of isobutylene in concentrated sulfuric acid polymerizes completely in about a minute. Poly(isobutylene) has numerous applications, including in caulking compounds, various adhesives, and chewing gum, but serving as a liquid fuel for spark-ignition engines is not one of them.

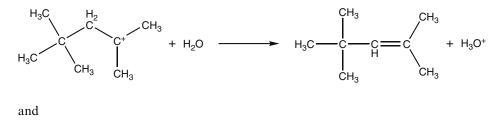
Isobutylene is obtained as part of the  $C_4$  cut of products from catalytic cracking. This fraction also includes other  $C_4$  compounds: 1-butene, 2-butene, butane, and 2-methylpropane (isobutane). The 60–65% sulfuric acid solution selectively absorbs isobutylene from the  $C_4$  cut. In the presence of the acid, the double bond is protonated to form a carbocation:



Protonation proceeds to form the most stable carbocation, the  $3^{\circ}$  ion shown above, rather than the  $1^{\circ}$  ion. Carbocations seek out and react with molecules having an apparent concentration of electron density, such as a double bond. Thus the *tert*-butyl carbocation reacts with a second molecule of isobutylene:



The product of the reaction is still a  $3^{\circ}$  carbocation. This new dimeric carbocation could, in principle, attack yet another molecule having a double bond. In the presence of some acid catalysts, such as anhydrous hydrogen fluoride or concentrated sulfuric acid, this is exactly what happens, giving poly(isobutylene). However, in 60–65% aqueous sulfuric acid, at 70 °C, the dimeric carbocation loses a proton to a water molecule:





Now, the reaction stops with dimerization. 2,4,4-Trimethyl-1-pentene accounts for  $\approx$ 80% of the product, and 2,4,4-trimethyl-2-pentene the remainder. These two isomers, also known as diisobutylenes, can be hydrogenated to the same product, 2,2,4-trimethylpentane. This is the standard of combustion performance in gasoline, with octane number of 100.

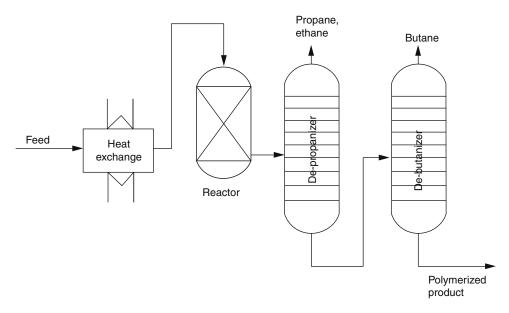
Production of branched-chain alkanes by dimerization can be a valuable route to increasing both yield and octane number of gasoline. In industrial practice, the feed is not a single pure compound, but usually a mixture of small alkenes. Propylene dimerizes to branched-chain hexanes, and propylene and isobutylene react to yield branched-chain heptanes. The product has octane numbers of 93–99.

Figure 14.4 shows a block flow diagram of an industrial polymerization process.

Depending on the specific feedstock and requirements for the product, reaction temperatures are 150–220 °C and pressures, 1–8 MPa. An example of a polymerization catalyst is phosphoric acid on a solid support, such as quartz or kieselguhr (a material also known as diatomaceous or infusorial earth, consisting of the silica shells of microscopic aquatic plants).

# 14.5 Catalytic cracking

Thermal cracking (Chapter 16) increases gasoline yield by breaking down molecules in less valuable fractions boiling above the gasoline range. Formation of alkenes, branchedchain aromatics, from recombination reactions of  $2^{\circ}$  radicals, and of aromatics, from internal hydrogen redistribution processes, contribute to increased octane numbers. Gasoline from thermal cracking might have octane numbers of  $\approx$ 75, but is not good enough for modern spark-ignition engines, which require 87–94 octane gasoline. The outbreak of the Second World War in 1939 greatly increased the demand for liquid fuels, one of which was aviation gasoline (avgas) having octane numbers >100.



**Figure 14.4** Process flow for a polymerization reaction, which combines small molecules that are normally gases into larger molecules in the gasoline range.

In the late 1930s, Eugene Houdry (Figure 14.5) [G], a French mechanical engineer, began to consider the possibility of using catalysts to improve the thermal cracking processes of that era. Houdry found that natural clay minerals not only caused an accelerated rate of cracking of tars or other heavy distillates, but also a marked shift in octane number, a result of the production of high concentrations of branched-chain alkanes.

## 14.5.1 Cracking catalysts

The key to enhancing both yield and octane rating of gasoline lies in breaking down large hydrocarbon molecules to produce compounds boiling in the gasoline range *and* converting straight-chains to branched-chains. Of crucial importance is that the cracking reaction proceed via carbocations rather than via radicals. To differentiate this process from the earlier, and now largely obsolete, thermal cracking processes, the term catalytic cracking denotes a process in which a catalyst is used to achieve both objectives in a single reaction process.

Carbocation generation occurs in two ways, hydride abstraction from an alkane, e.g.

$$CH_3CH_2CH_3 \rightarrow CH_3CH^+CH_3 + H^-,$$

or by protonation of an alkene, e.g.

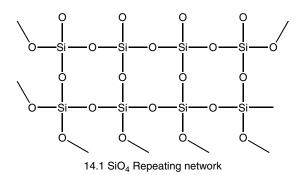
$$CH_3CH=CH_2 + H^+ \rightarrow CH_3CH^+CH_3.$$

A hydride ion with its pair of electrons acts as a Lewis base. Hydride abstraction therefore requires a good electron-pair acceptor, i.e. a Lewis acid. To protonate a weak base such as an alkene requires a good proton donor, i.e. a Brønsted acid. Ideally, both functions should be available in the same catalyst.

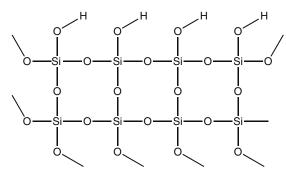


Figure 14.5 Eugene Houdry, inventor of catalytic cracking.

To consider how aluminosilicate materials can function as cracking catalysts, it is convenient to begin with silica itself. Silica has an infinite repeating network of  $SiO_4$  tetrahedra (14.1).

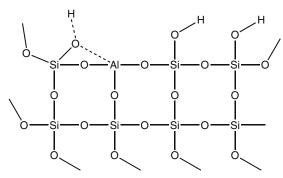


Even though the structure could be considered to be an infinite network of Si–O bonds, at some point a particle of silica has to have a surface. Oxygen atoms at the surface can incorporate hydrogen atoms (14.2).



14.2 SiO<sub>4</sub> surface showing protonated oxygen atoms

The –OH groups on the silica surface are very weak Brønsted acids. By itself, silica is not useful as a catalyst for the reactions of interest here. In fact, sometimes silica, as sand, finds use in reaction systems as an inert diluent. But, the structure can be modified by replacing some of the silicon atoms by aluminum atoms (14.3).

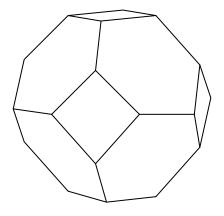


14.3 Modified structure with aluminum incorporation

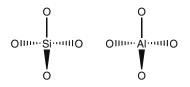
The aluminum atoms provide good Lewis acid sites. By interacting with the surface oxygen atoms, as implied by the dashed-line bonds in structure 14.3, aluminum atoms weaken the O–H bond and enhance the Brønsted acidity.

Neither silicon dioxide nor aluminum oxide (alumina) by themselves makes satisfactory cracking catalysts. Silica does not catalyze cracking. Alumina provides very high initial rates of cracking, but loses its activity quickly, so that further reactions do not occur. Neither does a simple mechanical mixture of the two compounds serve as a good catalyst. However, when silica and alumina comprise part of the same chemical structure, an active cracking catalyst can result. The first catalyst used in cracking was a naturally occurring clay mineral, montmorillonite [H]. It was replaced by a synthetic material containing 87% SiO<sub>2</sub> and 13% Al<sub>2</sub>O<sub>3</sub>. Nowadays most catalysts used in cracking are zeolites.

The zeolites are an enormous family of aluminosilicates. Many occur naturally, but synthetic zeolites have come to be preferred because their properties can be tailored for the specific job at hand. The basic structural units in zeolites are  $AlO_4$  and  $SiO_4$  tetrahedra (14.4).



**Figure 14.6** The sodalite structure is formed by linking  $AlO_4$  and  $SiO_4$  tetrahedra. The structure sketched here is a cuboctahedron, in which an aluminum or silicon atom is at each vertex. The cuboctahedra then link to produce zeolite structures.



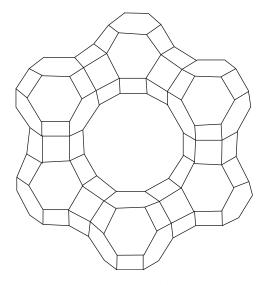
14.4 Basic zeolite structural units

These tetrahedra link together in three dimensions via Si–O–Si, Si–O–Al and Al–O–Al bonds to form the sodalite structure (Figure 14.6).

In the sodalite structure as sketched above, each vertex is occupied by a silicon or aluminum atom. Each edge is an M-O-M' bond, where M and M' are silicon or aluminum atoms. Each sodalite structure is, geometrically, a truncated octahedron. The interior is hollow on an atomic scale, so in a sense the sodalite truncated octahedron represents a "cage" that might accommodate atoms or small molecules.

The zeolite structure consists of sodalite "cages" linked to form a "supercage," see Figure 14.7, where each of the units represents one of the sodalite structures illustrated above. The truncated octahedra making up the sodalite structure are joined to form the zeolite structure (Figure 14.8).

Of the more than 30 naturally occurring zeolites, the most common are faujasite (Figure 14.9) and mordenite. A crystal lattice having only  $AlO_4$  structures would have a net negative charge, so zeolites also contain cations of the alkali and alkaline earth elements, particularly sodium, potassium, and calcium. These cations have some freedom of movement within the structure, and readily undergo ion-exchange processes [I]. Their success as catalysts has led to synthesis of numerous zeolites not found in nature. The properties of the synthetic zeolite, including the diameter of the pores, can be modified by changing the associated cations. For example, Type A synthetic zeolite, containing Na<sup>+</sup> ions, has a pore diameter of 0.4 nm, but if the Na<sup>+</sup> is replaced by K<sup>+</sup>, the pore openings are reduced to 0.3 nm. This helps to tailor the pore sizes of synthetic catalysts. The former Mobil Corporation, now ExxonMobil, was a leader in synthesis and development of new zeolite catalysts. About 95% of the catalytic cracking



**Figure 14.7** A representation of a zeolite structure, which can be thought of as being made by linking the individual sodalite structures shown in Figure 14.6. The large opening in the center of this representation leads to the so-called supercage.

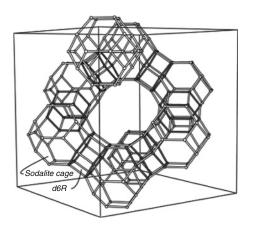


Figure 14.8 A model of the faujasite structure, showing the supercages linking up to form the overall structure.

units in refineries in the United States use zeolite catalysts that derive from Mobil's pioneering work.

Molecules encountering the catalyst access the supercage via "windows." The windows permit only molecules of selected sizes and shapes to enter the catalyst. For example, in a cracking catalyst, straight-chain alkanes can enter the windows, whereas the branched-chain alkanes, that would be preferred not to crack, cannot. Very large alkanes that cannot enter the windows react on the external surface of the catalyst. Their cracking products might then be small enough to enter the catalyst, where they can undergo further reactions. The volume of the supercage retains reactant molecules long enough for them to react while they are in the cage.

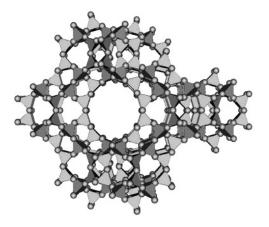


Figure 14.9 Faujasite, a naturally occurring zeolite with catalytic properties, has an open structure that allows transport of reactants into the supercages and products outward.

A typical catalyst consists of 3-25% of zeolite crystals, about 1 µm diameter, embedded in a matrix of silicon and aluminum oxides. The catalyst particles themselves, when used in fluidized-bed cracking units, are 20–60 µm diameter. The silica–alumina matrix is used for two reasons: zeolites are too expensive to permit use of pure zeolite particles on an industrial scale; and zeolites when used alone are such active catalysts that it would be hard to design practical industrial-scale reactors that could accommodate the heat transfer requirements for safe, satisfactory operation.

The superior activity of zeolites comes in part from a greater concentration of catalytically active sites on the zeolite surface, compared with a silica–alumina surface. Also, the porous structure of the zeolite allows a greater effective concentration of the molecules undergoing cracking in the vicinity of a catalytically active site than can be achieved on a silica–alumina catalyst. Further, zeolite catalysts produce more products in the desired gasoline range,  $C_5$ – $C_{10}$ , and fewer light  $C_3$ – $C_4$  products. The molecular size of the cracking products depends on a balance between cleavage of C–C bonds, and hydride transfer to stabilize carbocations. Compared to silica–alumina catalysts, zeolites have greater ability for hydride transfer relative to C–C bond cleavage. Consequently, cracking tends to stop at products with somewhat longer carbon chains when zeolite catalysts are used.

The balance between rate of C–C bond cleavage and hydride transfer is determined by the strength of the acid sites on the catalyst. A silica–alumina catalyst contains very strong acid sites. The molecule undergoing cracking is likely to be very strongly bound to the catalytically active site, and the cracking reaction is rapid. Cracking, in this case, can be much faster than hydride transfer. In comparison, the acid sites on a zeolite surface are weaker. Binding of molecules to these sites is weaker, and cracking is slow relative to hydride transfer.

A zeolite catalyst produces fewer alkenes than does a silica–alumina catalyst, because zeolites are the superior catalyst for transferring hydrogen to alkenes. Most alkenes formed during cracking become hydrogenated before they can desorb. Thus the alkene concentration in the product stream is relatively low. Hydride transfer to stabilize carbocations and hydrogen transfer to alkenes proceed at high rates on zeolite catalysts because of the greater effective concentration of molecules in the vicinity of an active site. The greater concentration is attained by having the reactions proceed in the small pores of the catalyst. The sequence of reactions from alkenes to alkadienes or alkatrienes and then to aromatics generates precursors for coke formation on catalyst surfaces. Since zeolites are effective at transferring hydrogen to alkenes, they also produce less coke than a silica–alumina catalyst.

Overall, zeolites have four important features: their structure results in a uniform pore size, rather than a distribution of pore sizes. The unique structure also results in high surface area and high pore volume. As with all catalysts, activity is controlled by the composition of the surface, but for zeolites surface composition can be changed by slight modifications to the synthetic procedure. The selectivity of zeolite catalysts derives from the regularity of their pore structure; selectivity can also be changed during the synthesis.

### 14.5.2 Cracking reactions

Cracking essentially is the reverse of polymerization or alkylation. Because energy is required to break a chemical bond, the enthalpy change for cracking is positive. And, because one large molecule generates two (or more) smaller ones, the entropy change is also positive. Since  $\Delta G = \Delta H - T\Delta S$ , and  $\Delta G$  must be negative for a reaction to be thermodynamically allowed, that condition can be met for positive values of  $\Delta H$  and  $\Delta S$  only if *T* is large enough for the  $-T\Delta S$  term to outweigh  $\Delta H$ . Thus thermodynamic considerations necessitate running cracking at high temperatures. Contrarily, in polymerization, bond formation results in a net negative  $\Delta H$ , and coupling of two small molecules into a larger one causes  $\Delta S$  to be negative as well. Thermodynamically, polymerization can be run at low temperatures, so long as they are consistent with acceptably high reaction rates.

Presuming a feedstock rich in alkanes, hydride abstraction occurs on a Lewis acid site on the catalyst:

# $\label{eq:ch_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3} \begin{array}{l} \rightarrow \\ CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + H^-. \end{array}$

(For convenience, decane is used as an example of the feedstock; in actual catalytic cracking processes the feed will be much larger than  $C_{10}$ .) Fragmentation of the molecule occurs via  $\beta$ -bond scission, thus

$$CH_{3}CH_{2}CH_{2}CH_{2}CH^{+}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3} \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH = CH_{2}+^{+}CH_{2}CH_{2}CH_{2}CH_{3}.$$

 $\beta$ -bond scission usually occurs so that the smaller fragment contains at least three carbon atoms. Protonation of the alkene occurs on a Brønsted acid site:

$$CH_3CH_2CH_2CH_2CH = CH_2 + H^+ \rightarrow CH_3CH_2CH_2CH_2CH^+CH_3.$$

The 1° carbocation formed in the  $\beta$ -bond scission reaction rearranges to the more stable 2° or 3° ions. Both carbocations can undergo further  $\beta$ -bond scission reactions, the

products of which react further by continued protonation and rearrangement. The sequence of protonations,  $\beta$ -bond scissions, and rearrangements continues until fragments of about six to eight carbon atoms are produced. Final stabilization of the carbocation occurs by returning the hydride ion from the Lewis acid site on the catalyst to the carbocation:

#### $CH_3CH_2CH_2CH_2CH^+CH_3 + H^- \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3.$

 $\beta$ -bond scission accounts for cracking, but not for chain branching. Chain branching isomerization derives from the order of stability of carbocations:  $3^{\circ} > 2^{\circ} > 1^{\circ}$ . As an example, a  $2^{\circ}$  carbocation rearranges to a  $3^{\circ}$  ion:

# $CH_3CH^+CH_2CH_3 \rightarrow (CH_3)_3C^+.$

When these reactions occur with molecules boiling in the gasoline range, they serve to increase octane number. Multiple isomerizations can occur, e.g.

$$H_{3}C - CH_{2} - CH_{2} - CH_{2} - CH_{2} - CH_{3} \longrightarrow H_{3}C - CH_{2} - CH_{2} - CH_{2} - CH_{3} \longrightarrow H_{3}C - CH_{3} - C$$

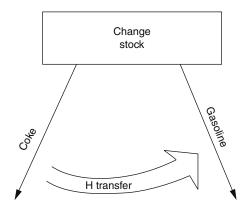
Branched-chain alkanes and cycloalkanes crack more rapidly than do straightchain alkanes. As a rule,  $3^{\circ}$  carbon-atom sites are about ten times as reactive as  $2^{\circ}$  carbon atoms, and about twenty times as reactive as  $1^{\circ}$  carbon atoms. For straight-chain alkanes, the longer the carbon chain, the higher the rate of cracking. Molecules having longer carbon chains will cover more of the catalyst surface; the greater the surface coverage of the catalyst, the higher the rate of carbocation formation. For example, octadecane cracks about 20 times faster on a zeolite surface than does octane.

The importance of  $\beta$ -bond scission in catalytic cracking would make it reasonable to expect roughly equal amounts of alkanes and alkenes in the product. In practice, catalytic cracking over zeolites results in products nearly free of alkenes, due to rapid hydrogen transfer from cycloalkanes and cycloalkenes, converting alkenes to alkanes, and producing aromatics from cycloalkanes. Hydrogen transfer seems to occur directly from the compound donating the hydrogen and the alkene. For example, passing decahydronaphthalene (decalin) over a cracking catalyst does not liberate hydrogen; nor does passing a mixture of hydrogen and an alkene over such a catalyst. But, using a feed of decalin and an alkene converts the alkene to an alkane.

During catalytic cracking, side reactions involving hydrogen redistribution also occur. The benefit of a reaction such as this one, for the hypothetical transfer of hydrogen from a cycloalkane to an alkene:



derives from the very high octane numbers of small aromatic molecules. Unfortunately, aromatics have other characteristics, as noted previously, that require their concentration in gasoline to be limited.

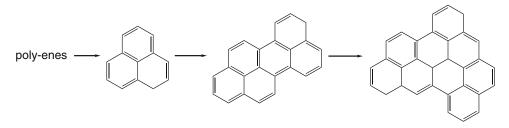


**Figure 14.10** Catalytic cracking produces liquids that are more hydrogen-rich than the charge stock. Doing so involves a redistribution of hydrogen within the system, also resulting in the carbon-rich product, coke.

Hydrogen transfer between alkenes can produce di-, tri-, or poly-enes:



This example could, with larger molecules, proceed to products with even greater degrees of unsaturation, i.e. to tri-enes and poly-enes. Hydrogenation is important for stabilizing alkenes, but also because dienes or trienes formed by hydrogen transfer between alkenes are precursors to coke formation, e.g.



The process is another manifestation of internal hydrogen redistribution (Figure 14.10).

These reactions lead to build-up of coke on the catalyst surface. Coke formation represents the "carbon-rich" side of the hydrogen redistribution processes. Hydrogen transferred to the hydrogen-rich side is used for hydrogenation of alkenes to alkanes and for stabilization of carbocations. Problems caused by coking include the gradual destruction of activity by the coke covering the catalyst surface and blocking pores, and the need for a separate processing step to regenerate the catalyst by burn-off of the coke. However, catalyst coking is exothermic, the heat liberated being used to help drive the endothermic cracking reactions.

#### 14.5.3 Practical aspects

Three factors determine the extent of cracking, hydrogen transfer, and isomerization: the chemical structure of the catalyst, which in turn determines the strengths of the Lewis and Brønsted sites on the surface; physical structure of the catalyst, which

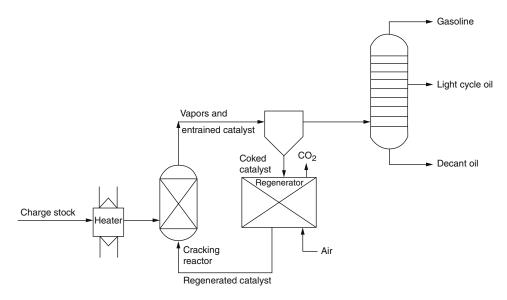


Figure 14.11 Process flow for a catalytic cracking process.

determines the access of the cracking stock to the surface, including the internal surface in pores; and the reaction conditions, pressure, temperature, and residence time.

The problem of coke formation was solved by Warren Lewis and Edwin Gilliland [J], who developed a system of two parallel fluidized-bed units. In one reactor, catalytic cracking occurs, while the other unit serves to burn coke off the catalyst. Fluid catalytic cracking (FCC) is now the second-most important process in a refinery, after distillation. FCC provides both the gasoline yield and the octane rating needed to meet today's market demand. The original site of the commercialization of catalytic cracking, the Marcus Hook, Pennsylvania refinery of what was then the Sun Oil Company, has been designated a National Historical Chemical Landmark by the American Chemical Society. Some historians of technology have suggested that the development of the FCC process is the greatest triumph of chemical engineering in the twentieth century.

A fluid catalytic cracking process is represented by the flow diagram in Figure 14.11. Not all potential cracking stocks are equally useful for optimum performance in catalytic cracking. Some feeds have high tendencies to form cokes. Others may contain sufficient amounts of trace elements, notably nickel and vanadium, to poison the catalyst. Feeds with high nitrogen content are also undesirable, since many organic nitrogen compounds are basic, and could poison the catalyst by adsorbing very tightly to the active acidic sites. A typical feedstock to fluid catalytic cracking is heavy gas oil. The products include: gases, ethylene, and LPG; the desired high-octane gasoline; and a heavier distillate product, light cycle oil. Additionally, a slurry of catalyst in a heavy, aromatic liquid is taken from the reactor. Separating the catalyst itself from the heavy oil by decantation produces, as the liquid product, a material called clarified slurry oil or decant oil. Decant oil can be a premium feedstock for delayed coking (Chapter 16), especially for production of premiumquality needle coke for eventual conversion to synthetic graphite (Chapter 24).

Catalytic cracking commonly uses fluidized-bed units in which hot vapor of the cracking stock (e.g. heavy gas oil) is passed through a bed of catalyst particles. Fluidization insures an intimate contact of the cracking stock vapor with the catalyst particles.

Typical process conditions are 465-540 °C, 0.2-0.4 MPa, with a catalyst-to-vapor weight ratio of 5-20. About 80% of all gasoline is produced by cracking, and 85-90% of cracking processes use catalytic cracking.

# 14.6 Catalytic reforming

Molecular structural changes that could be beneficial in enhancing octane number include: isomerization of straight-chain to branched-chain structures; dehydrocyclization of alkanes to cycloalkanes; ring enlargement of alkylated cyclopentanes to cyclohexanes; and dehydrogenation of cycloalkanes to aromatics. In these reactions, the total number of carbon atoms in the molecule does not change. The shape, or form, of molecules changes. Since the molecules are being re-shaped or re-formed, these processes collectively can be called reforming processes. Their chemistry differs greatly from the process of steam reforming (Chapter 19). Because of the need to emphasize a different chemistry from steam reforming, and the fact that reforming to enhance octane number relies on special catalysts, these processes are known as catalytic reforming.

If needed, the heavy naphtha feedstock used for catalytic cracking can be treated with hydrogen to reduce the sulfur content. This process, hydrodesulfurization, is discussed in Chapter 15. Hydrodesulfurization of the heavy naphtha upstream of the catalytic reforming unit protects the reforming catalyst from poisoning by sulfur.

## 14.6.1 Reforming catalysts

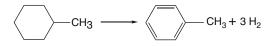
Zeolites are usually not used in reforming because they are very active cracking catalysts; here, the goal is not to crack molecules but rather to re-form them. Some reforming processes, such as isomerization, involve changing the shape of the carbon skeleton. Others involve moving hydrogen into, or out of, molecules, e.g. dehydrogenation. The catalyst used in catalytic reforming has to be capable of doing two jobs: isomerizing carbon skeletons, and adding or removing hydrogen. Catalysts able to facilitate two somewhat different reactions are called bifunctional catalysts, or sometimes dual-function catalysts.

A typical reforming catalyst contains a metal to move hydrogen into or out of molecules, and an acidic oxide to facilitate structural rearrangement. The metallic portion of the bifunctional catalyst is a transition metal. Many transition metals do a good job of adsorbing hydrogen and hydrocarbon molecules. These metals have the desirable characteristics of being able to coordinate with double bonds, and adsorbing and dissociating hydrogen. Nickel, palladium, and platinum are among the best. Other platinum-group metals, such as iridium, rhodium, and ruthenium, also make excellent catalysts, but are not used so often in commercial practice. All of these metals are poisoned by organosulfur compounds, which form strong bonds with the metal atoms on the surface, making it unavailable to hydrogen or hydrocarbons. When platinum is used, the reforming process is sometimes known as platforming. In current technology platinum is alloyed with rhenium to reduce the rate of coking on the surface.

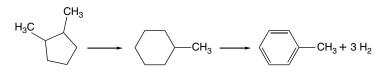
The metal adsorbs and dissociates hydrogen. Since a catalyst affects reaction kinetics, and not thermodynamics, it affects the rates of both forward and reverse reactions. A substance that catalyzes the reaction  $A \rightarrow B$  will also catalyze  $B \rightarrow A$ . In the context of catalytic reforming, a metal hydrogenation catalyst is also a dehydrogenation catalyst. The ability of the metal to remove *or* add hydrogen provides a route from alkane to alkene to new alkane.

#### 14.6.2 Reforming reactions

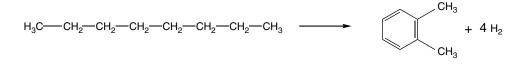
At least six reactions occur in the process of catalytic reforming. Dehydrogenation of cycloalkanes converts them to aromatics:



Dehydroisomerization of cycloalkanes converts an alkylcyclopentane, via cyclohexane derivatives, to alkylaromatics:



Dehydrocyclization of alkanes forms cycloalkanes or goes all the way to aromatics:

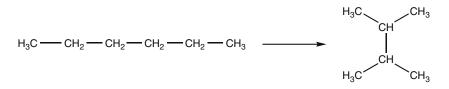


If the feed did not pass through a hydrodesulfurization step upstream, or if some sulfur compounds remain, hydrodesulfurization occurs in the catalytic reforming process:

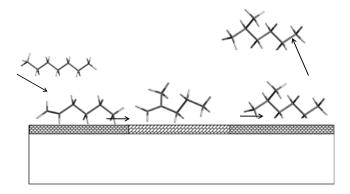
$$H_3C - CH_2 - CH_2 - CH_3 + H_2S$$

Two additional, important reactions – isomerization and hydrocracking of alkanes – are discussed in more detail below. Each of these six reactions, in its own way, improves the product of catalytic reforming. Branched-chain alkanes and aromatics raise the octane number. Loss of sulfur is almost always an improvement.

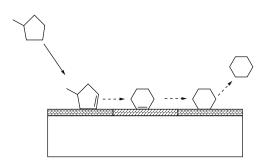
Isomerization of *n*-alkanes creates the desired branched-chain alkanes, e.g.



Isomerization is illustrated in Figure 14.12 for hexane. It involves three steps on the catalyst surface. Hexane loses hydrogen to the metal to form 1-hexene. On the acidic oxide surface, 1-hexene rearranges to 2-methyl-1-pentene. Then, 2-methyl-1-pentene regains hydrogen from the metal to form the desired product 2-methylpentane (isohexane). Other reactions involve sequences of flow of hydrogen to the metallic component of the catalyst, formation and rearrangement of a carbocation on the acidic



**Figure 14.12** The isomerization of hexane to 2-methylpentane (isohexane) during catalytic reforming proceeds via an alkene intermediate.

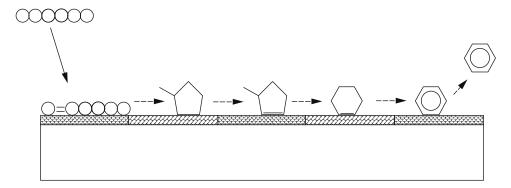


**Figure 14.13** The ring-expansion isomerization of methylcyclopentane to cyclohexane during catalytic reforming proceeds via formation of a cyclopentene intermediate.

component, and further gain or loss of hydrogen on the metal surface. For example, reforming of methylcyclopentane (Figure 14.13) begins with dehydrogenation to methylcyclopentene, followed by ring expansion on the acidic surface to cyclohexene, and finally hydrogenation on the metal surface to cyclohexane. Conversion of hexane to benzene, see Figure 14.14, involves similar processes. In this case, the 1-hexene formed on the metal surface isomerizes to methylcyclopentane, which then converts to cyclohexene, the cyclohexene in turn dehydrogenating to benzene.

The only process in which the dual functionality of the catalyst is not important is dehydrogenation of cycloalkanes to aromatics, involving only loss of hydrogen. For cyclohexane, as an example, dehydrogenation begins with initial adsorption onto the catalyst. Loss of six hydrogen atoms is very rapid, possibly even simultaneous. Interactions of the  $\pi$  electrons in benzene with the *d* orbitals on the metal atoms helps hold the benzene product to the catalyst surface.

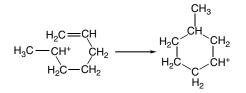
Alkane isomerization requires hydride abstraction to generate a carbocation, a more difficult reaction than alkene isomerization, which depends on protonation of a double bond. Alkane isomerization can be facilitated by adding small amounts of related alkenes to the feed. Carbocations formed by alkene protonation participate in intermolecular hydride transfer reactions with alkanes, thereby increasing the rate. Alkane isomerization also occurs on the metal sites



**Figure 14.14** The cyclization and dehydrogenation of hexane to produce benzene during catalytic reforming is a multistep process involving alkenes, cycloalkanes, and cycloalkenes as intermediates.

on the catalyst, the way in which the alkane adsorbs onto the catalyst being critical. Adsorption of an alkane on the metal surface sites via two adjacent carbon atom positions could result in loss of hydrogen to the catalyst, forming an alkene. The alkene could desorb without experiencing re-hydrogenation, nor undergoing isomerization. But, if the original alkane adsorbs through two carbon atoms that are four or five positions distant from each other in the chain, loss of hydrogen to the metal sites and formation of a new C–C bond results not in alkene formation but rather in ring-closure to an alkylcyclopentane or alkylcyclohexane. If these cycloalkanes remain on the catalyst, further reactions could occur, such as dehydrogenation to alkylbenzenes, or readsorption on the catalyst and ring opening by C–C bond cleavage to produce branched-chain alkanes. Depending on the sequence of events on the catalyst surface, *n*-alkanes can be converted to branched-chain alkanes, alkylcycloalkanes, or alkylaromatics.

Alkenes undergo various reactions during catalytic reforming, including hydrogenation to alkanes, isomerization and hydrogenation to branched-chain alkanes, or cyclization to cycloalkanes. Ring closure in alkenes can be regarded as a "self-alkylation" process, analogous to alkylation described above. In this case both the carbocation and the double bond are part of the same molecule:



This process can also be considered to be the reverse of a  $\beta$ -bond scission reaction. Cyclic carbocations, like the one illustrated above, can transfer a proton to an alkene, being converted to a cycloalkene. Loss of a hydride from the cycloalkene forms a cycloalkenyl carbocation. A continuing sequence of reactions leads to formation of cycloalkadienes, and eventually to aromatics.

High concentrations of alkenes in the feed are undesirable, consuming large amounts of hydrogen, or dehydrogenating to highly unsaturated precursors to coke. If a reforming feedstock contains large amounts of alkenes, it may be useful to reduce their concentration in a separate hydrogenation step upstream of catalytic reforming.

*n*-Alkanes larger than those in gasoline can undergo hydrocracking. In this reaction, the cracked fragments are stabilized by hydrogen, so that alkene formation does not occur to any significant extent. Isomerization to branched-chain alkanes can also occur in hydrocracking:

$$n - C_{16}H_{34} + H_2 \longrightarrow 2 CH - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$
  
 $H_3C$ 

While this example shows formation of two molecules of iso-octane, hydrocracking can, and often does, lead to two dissimilar products. Hydrocracking begins with adsorption of two adjacent carbon atoms on the catalyst surface, with subsequent breaking of C–H bonds on these atoms. Further loss of hydrogen from the two affected carbon atoms results in formation of carbon–metal double or triple bonds. Formation of these strong, multiple carbon–metal bonds cleaves the C–C bond between the two adsorbed atoms. Subsequent addition of hydrogen to the two fragments forms two smaller alkane molecules. The actual position along the carbon chain at which hydrocracking occurs depends on the catalyst. Nickel favors hydrocracking to methane, i.e. cleaving a terminal C–C bond, while platinum favors hydrocracking in the interior of the chain. Hydrocracking requires high temperatures and metals that form very strong carbon–metal bonds. Both straight- and branched-chain alkanes can undergo hydrocracking.

The rate of hydrocracking increases very rapidly as a function of the number of carbon atoms in the reacting species. For example, hexadecane cracks about three times as rapidly as dodecane. The strong dependence of cracking rates on molecular weight is useful in practice. Undesirable long-chain alkanes are "cracked out" of the feedstock, while the more desirable shorter-chain compounds, which undergo hydrocracking much more slowly, tend to survive into the product stream.

#### 14.6.3 Practical aspects

Feedstocks for catalytic reforming are usually straight-run naphthas, or low-octane liquids (<50 octane) from thermal cracking processes. High concentrations of alkenes are undesirable because their further dehydrogenation leads to polycyclic aromatics, precursors to coke. Nitrogen and sulfur compounds are undesirable because they act as catalyst poisons. Sulfur compounds can also cause corrosion of metal components of reactors and piping.

Catalytic reforming produces desirable branched-chain or cyclic structures without attendant cracking. Reforming is a net endothermic process. Reaction temperatures are 450–500 °C. If the temperature drops, reaction rates become unacceptably slow. Often hydrogen is added with the feed to suppress coke formation and to prevent "over-

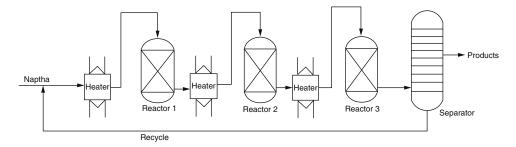


Figure 14.15 Process flow for a three-stage catalytic reforming operation.

aromatization," i.e. the production of too high a proportion of aromatic compounds in the product. A platinum–rhenium alloy supported on alumina is a favored catalyst. The catalyst is partially sulfided prior to use, because both rhenium and sulfur seem to have roles in reducing coke formation.

Figure 14.15 shows a block-flow diagram of a typical catalytic reforming process. In a process like this, the feed could be a paraffinic, straight-run naphtha of <50 octane. Because of the overall endothermicity of catalytic reforming and the need to run at high temperature to achieve acceptable rates, reforming is typically carried out in a sequence of reactors with external heating between each reactor. Overall, a process of this type can convert 38-octane naphtha to 90-octane gasoline. Table 14.2 summarizes the performance.

Some reforming reactions involve adding hydrogen to molecules; others involve removal of hydrogen. Thus hydrogen partial pressure plays an important role in determining the nature of the products. At low hydrogen partial pressures, the equilibrium between cycloalkanes and aromatics favors aromatics. By extension, a low hydrogen partial pressure favors coke formation, since aromatics are the precursors to cokes. High hydrogen partial pressure favors hydrocracking and decreases formation of aromatics and coke. The choice of hydrogen partial pressure represents a compromise among hydrocracking, aromatics production, and catalyst deactivation; values of hydrogen partial pressure and operating temperature establish the rate of catalyst deactivation by coking. A typical total pressure in the reactor would be  $\approx 2$  MPa.

High-temperature operation leads to rapid catalyst deactivation. Low temperatures result in low reaction rates, but on the other hand shift equilibrium to favor cycloalk-anes rather than aromatics. Temperature control to within, say,  $\pm 20$  °C is desirable.

As in catalytic cracking, coke formation on the catalyst is a problem. Coke formation occurs more readily on the oxide surfaces than on the metal surfaces, because it associates more with carbocation formation than with hydrogenation-dehydrogenation reactions. A coked catalyst can be regenerated by carefully burning off the coke at, e.g.  $450 \,^{\circ}$ C in an atmosphere of  $\approx 1\%$  oxygen.

The catalytic reforming product, called reformate, becomes part of the gasoline pool in the refinery. In a large refinery, gasoline might be produced in several processes: catalytic cracking, catalytic reforming, alkylation, polymerization, distillation (i.e. straight-run gasoline or light naphtha), and from thermal processes (Chapter 16). Several, or all, of these processes running in a refinery produce gasolines of various qualities. All of these products are considered blending stocks to be used to produce, via

	Stage		
	1	2	3
Inlet temperature, °C	500	500	500
Outlet temperature, °C	430	470	495
Octane number of product,	66	80	90
Percent of total catalyst used in this stage	15	35	50
Principal reactions occurring in this stage	A, B	A, B, C, D	C, D

**Table 14.2** Performance of three-stage catalytic reforming of naphtha. The dominant reactions are indicated as: A, dehydrogenation; B, dehydroisomerization; C, hydrocracking; and D, dehydrocyclization.

blending steps, gasoline meeting market specifications. These blending products are ultimately what reach the consumers.

# 14.7 Methanol to gasoline

Processes discussed in the previous sections all began with petroleum-derived feedstocks, and, through manipulation of molecular sizes and shapes, produce hydrocarbon-based gasolines. Many, sometimes all, of these processes can be found in most modern refineries, and constitute part of the traditional practice of petroleum refining. Other, non-traditional catalytic routes to hydrocarbon-based gasoline also exist. They may become of increasing importance as petroleum becomes less available, or in a recurrence of geopolitically induced oil shortages, such as occurred in the 1970s. One such process, conversion of methanol to gasoline, is discussed in this section. A second process, the Fischer–Tropsch synthesis, has a much broader application than the production only of gasoline, and is discussed in Chapter 21. Of course, non-hydrocarbon liquid fuels, especially the smaller alcohols, may also become important in the future.

Methanol has some attractive features as a fuel for spark-ignition engines. It has a very high octane number, 133 (RON), making it suitable for use in high-performance, high-compression engines. Though currently almost all methanol is made from natural gas, it can be produced from biomass gasification followed by methanol synthesis (Chapter 21). In that regard, methanol is, at least partially, a renewable fuel. On the other hand, significant concerns about methanol also exist. It has about half the volumetric energy density of gasoline, thus giving about half the fuel economy for vehicles of comparable size and driving conditions. It is infinitely miscible with water, requiring precautions in storage, handling, and distribution, and representing a potential water-pollution threat in the event of a large spill. Its health hazards, if ingested or absorbed through the skin, include the possibility of permanent blindness. Concerns about these potential disadvantages of methanol can be eliminated by converting it to a mixture of hydrocarbons virtually identical with petroleum-derived gasoline.

If it were to be implemented today, the methanol-to-gasoline (MTG) process would probably begin with steam reforming of natural gas, followed by methanol synthesis. However, the extraordinary versatility of synthesis gas production, shift, and reaction

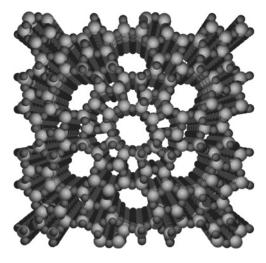


Figure 14.16 The ZSM-5 catalyst, which can be used in the methanol-to-gasoline process.

means that in the future other feedstocks, including coal, waste products, and biomass, could be used at the front end of an MTG plant. In principle, almost any carboncontaining raw material can be converted to a mixture of carbon monoxide and hydrogen, and from there to methanol. As a potential source of alternative liquid fuels in the near-term future, MTG has other advantages. First, an enormous infrastructure worldwide is already in place for manufacturing methanol. Today, large methanol plants have outputs up to five thousand tonnes per day. Second, the methanol synthesis units and the MTG process plant do not necessarily have to be co-located. Of course, doing so would reduce the need for methanol transport from one plant to the other, and is likely to achieve other economies, such as shared utilities. Nevertheless, in the event of a real, or politically created, energy crisis, methanol production could in principle be diverted from chemical markets into gasoline production.

The MTG process uses a special zeolite catalyst called ZSM-5 (for Zeolite–Sucony– Mobil, the companies involved in its development). A structure is shown in Figure 14.16.

ZSM-5 converts oxygenated compounds to hydrocarbons. As with other zeolites, ZSM-5 will only allow molecules of certain size and shape to enter or exit the pores where the catalyzed reactions take place. ZSM-5 has pore openings of about 0.6 nm diameter. Only  $C_{10}$  or smaller compounds can move through the structure of this zeolite. Molecules that form in the catalyst but are larger than  $C_{10}$  crack. As a result, ZSM-5 gives a narrow distribution of products, with about 80% being in the gasoline range,  $C_5$ – $C_{10}$ .

Methanol is converted to ethylene via dimethyl ether:

$$\label{eq:ch3OH} \begin{array}{l} 2 CH_3OH \rightarrow CH_3OCH_3 + H_2O, \\ \\ CH_3OCH_3 \rightarrow CH_2 = CH_2 + H_2O. \end{array}$$

Formation of dimethyl ether [K] proceeds at 300–325 °C and 2.3 MPa. Ethylene reacts further with methanol to form propylene:

$$CH_2 = CH_2 + CH_3OH \rightarrow CH_3CH = CH_2 + H_2O.$$

Conversion of dimethyl ether to gasoline occurs at 330–400 °C and 2.2 MPa over ZSM-5. Gasoline formation is exothermic ( $\Delta H$  is -75 kJ/mol at 427 °C). Exothermic reactions on acidic catalysts can lead to excessive coking, particularly in fixed-bed reactors. In the MTG process this problem is solved in part by carrying out the synthesis in two stages. Some of the product is recycled through the second-stage reactor for temperature control.

Formation of alkenes in the presence of an acidic catalyst (i.e. the zeolite) provides the opportunity for "polymerization" reactions to occur, similar to those discussed earlier in this chapter:

$$\label{eq:CH3CH} \begin{split} CH_3CH &= CH_2 + H^+ \rightarrow CH_3C^+HCH_3, \\ CH_3C^+HCH_3 + CH_3CH &= CH_2 \rightarrow (CH_3)_2CHCH_2C^+HCH_3, \\ (CH_3)_2CHCH_2C^+HCH_3 \rightarrow (CH_3)_2CHCH &= CHCH_3 + H^+. \end{split}$$

Once alkenes, 2-methyl-3-pentene in this example, have formed, they can react further to produce alkanes, cycloalkanes, and aromatics, in reactions similar to those already discussed. Many factors affect the specific product distribution, including the usual ones of temperature, pressure, and nature of the catalyst (specifically, its Si/Al ratio). The size of the "windows" in the zeolite catalyst is critical in forming products in the gasoline range of molecular sizes. Windows too small favor formation of ethylene; windows too large favor production of  $C_{10}^+$  compounds. Nevertheless, the principal products are branched-chain alkanes, and alkylaromatics, up to the size of 1,2,4,5-tetramethylbenzene (durene). These kinds of compound result in a high octane rating for the gasoline. With ZSM-5, a typical product distribution would be 2% C<sub>6</sub>, 16% C<sub>7</sub>, 39% C<sub>8</sub>, 28% C<sub>9</sub>, and 13% C<sub>10</sub>.

The largest-scale experience with the MTG process took place in New Zealand from 1985 to the mid-1990s. A plant was started up to take advantage of large offshore deposits of natural gas. The plant operated successfully with a capacity of about two thousand tonnes per day. Operation ceased when the worldwide price of oil was very low in the 1990s, the plant being a victim of economics and not of any problems with the technology.

## Notes

- [A] As mentioned in Chapter 12, there is no consistent set of terminology for various petroleum fractions, and there is some overlap of boiling ranges. A material boiling in the range from the initial boiling point to 150 °C is known as light naphtha, and from 150–205 °C as heavy naphtha.
- [B] Nikolaus Otto (1832–1891) had little or no formal training in engineering. He began his career as a traveling salesman. He learned about an engine developed by the French engineer Étienne Lenoir, which was designed to operate on natural gas. Otto got the idea that it would be more practical to use liquid gasoline as the fuel. He eventually started his own company, and hired some exceptionally talented engineers and designers to work for him, notably Wilhelm Maybach and Gottlieb Daimler, both of whom had major roles of their own in the history of automobiles and their engines. Otto's son, Gustav, founded the company Bayerische Motoren Werke AG, which is now known worldwide as BMW.

- [C] The smaller aromatic molecules have high octane numbers. Setting any other considerations aside, they would be excellent components of gasolines. However, many such compounds are suspect or proven carcinogens. Regulations on permissible gasoline quality strictly limit the aromatic content, and especially that of benzene. It has been claimed that, in years before the health hazards of these aromatics were appreciated, some companies added benzene to gasoline as an octane-enhancer.
- [D] The absolutely most reliable source of information on what grade of gasoline is best for your vehicle is the owner's manual. The general topic area of how different brands and grades of gasoline impact engine performance and longevity is awash in anecdotal reports and hearsay information, much of which bears little relationship to reality.
- [E] The term "smog" originated as a portmanteau word, a combination of smoke and fog. As discussed in notes D and E of Chapter 11, though the word nowadays is used as being synonymous with photochemical smog, other kinds of smog are known. Most notorious is sulfuric-acid smog, a problem once associated with coal combustion, when oxides of sulfur emitted to the atmosphere reacted with water in fog droplets to condense to a layer of sulfuric acid on particles of ash or partially burned coal in smoke. Sulfuric-acid smog is genuinely lethal, as shown in air pollution disasters in London and in Donora, Pennsylvania. Fortunately, the near-elimination of coal as a domestic fuel and the imposition of sulfur emission regulations in most industrialized nations has virtually eliminated the problem of sulfuric-acid smogs.
- [F] Propene, or propylene, is probably second only to ethylene in its importance as an organic chemical feedstock. Among the numerous products made from it are: polypropylene, a widely used plastic; propylene glycol, a component of antifreeze; and acrylonitrile, a monomer for production of acrylics and carbon fibers. 2-Methylpropene, or isobutylene, is used to make, as examples, a synthetic rubber called butyl rubber, and a family of antioxidants for food preservation, such as 2-*tert*-butyl-4-methoxyphenol (butylated hydroxy anisole, or BHA).
- [G] Eugene Houdry (1892–1962) was a much-decorated hero of World War I, for his service in the French tank corps. After the war he became quite interested in race cars, particularly improved fuels for racing. In France, he worked on conversion of coal tar to gasoline, and found silica-alumina catalysts that were promising. After the successful commercialization of the Houdry catalytic cracking process (in 1937, at the Sunoco refinery in Marcus Hook, Pennsylvania), Houdry continued working on catalysts. In the early 1950s, as smog began to envelop Los Angeles, Houdry invented what was essentially the first catalytic converter for automobile exhaust systems. Through no fault of Houdry's, catalytic converters did not become practical until lead additives were eliminated from gasoline in the United States in the late 1970s. Houdry's interests in catalysis extended to the action of enzymes, and in particular how enzymatic catalysis is affected in persons suffering from cancer.
- [H] Montmorillonite gives its name to a group of clay minerals whose formula is based on  $Al_2Si_4O_{10}(OH)_2$ . In the individual clays, a deficiency in  $Al^{+3}$  ions is accommodated by substitution of some alkali and alkaline earth cations, e.g.  $Na^+$  and  $Ca^{+2}$ , to maintain charge balance. The composition of montmorillonite itself is sometimes represented as  $Na_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$ .

- [I] Zeolites have been used since the 1930s for water softening, exchanging  $Ca^{+2}$  or  $Mg^{+2}$  from the water for Na<sup>+</sup>. Some laundry detergents contain a zeolite that will exchange Na<sup>+</sup>, to help soften the water during washing. Other zeolites have excellent selectivity for removing strontium and cesium, which makes them very useful in treating wastewaters that might contain the radioactive isotopes of these two elements,  ${}^{90}$ Sr and  ${}^{137}$ Cs.
- [J] Warren Lewis (1882–1975) was the first head of the Chemical Engineering Department at the Massachusetts Institute of Technology. Lewis is considered to be the "father of chemical engineering." His many accomplishments in research and education include establishing the subject of unit operations within chemical engineering. Edwin Gilliland (1909–1973), also at MIT for most of his career, also held numerous distinguished positions in public service, culminating with being a member of the President's Science Advisory Committee under Presidents Kennedy and Johnson.
- [K] Dimethyl ether (DME) is itself a potentially very useful fuel, though it is a gas at ambient conditions. DME has a cetane number of 55, which is somewhat higher than most petroleum-derived diesel fuels. DME has also been tested in blends with LPG as a fuel for spark-ignition engines. Its production is quite straightforward, involving dehydration of methanol:  $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ , usually in the presence of acid. Supposedly, a blend of DME and propane is available in some parts of the world as an over-the-counter treatment for warts, so that people can remove them at home by freezing them. It would be wise not to try smoking at the same time!

#### **Recommended reading**

- Gates, Bruce C., Katzer, James R., and Schuit, G.C.A. *Chemistry of Catalytic Processes*. McGraw-Hill: New York, 1979. This book remains a very useful discussion of practical aspects of catalysis. Chapters 1 and 3 are relevant to the material in this chapter.
- Guibet, Jean-Claude. *Fuels and Engines*. Éditions Technip: Paris, 1999. An excellent reference source, covering virtually every kind of fuel that might be burned in an internal-combustion engine. Chapter 3 is particularly relevant here.
- Jones, D. Stan. *Elements of Petroleum Processing*. Wiley: Chichester, 1995. A useful book covering practically all aspects of refinery operation. Chapters 9, 11, and 14 are relevant to the present chapter.
- Little, Donald M. *Catalytic Reforming*. PennWell: Tulsa, OK, 1985. This book covers most aspects of this process, including feed preparation, the catalyst, and the effects of process variables.
- Meyers, R.A. *Handbook of Petroleum Refining Processes*. McGraw-Hill: New York, 1997. This book has a wealth of detail on selected processes involved in refining. Parts 1, 3, and 4 are of particular relevance to this chapter.
- Sadeghbeigi, Reza. *Fluid Catalytic Cracking*. Gulf Publishing: Houston, 1995. This book has a greater emphasis on the practical aspects of FCC, such as design and operation of various FCC units.
- Speight, James G. *The Chemistry and Technology of Petroleum*. Marcel Dekker: New York, 1991. Chapters 15 and 17 of this comprehensive treatise relate to the present chapter.

Jet fuel, diesel fuel, and the lighter grades of fuel oil are collectively referred to as middle distillate fuels, from the fact that they are taken off the middle of a distillation column, below the light ends, such as gasoline and naphtha, and above the heavy ends and resids.

# 15.1 Middle distillate fuel products

# 15.1.1 Kerosene

Today, most kerosene is refined further into jet fuel. Kerosene itself continues to have some market in domestic space heaters, lights and stoves for camping, and occasionally as a light grade of fuel for diesel engines, "power kerosene."

Highly paraffinic Penn-grade oil makes excellent straight-run kerosene. Its original uses as fuel for domestic heating and lighting, require minimal sulfur content, because of odor, and low aromatics, to avoid smoke and soot formation. A typical boiling range for straight-run kerosene is 205-260 °C, indicating that the dominant components would be alkanes in the C<sub>12</sub>-C<sub>15</sub> range, alkylcyclohexanes, and alkylbenzenes. Derivatives of decalin, naphthalene, or larger compounds could be in solution at low concentrations.

In addition to boiling range and sulfur content, other important properties of kerosene are its flash point and cloud point. Flash point gives some indication of safety in storage and handling. The flash points of various kerosenes vary widely, but all are above normal ambient temperatures, e.g. 45 °C. Kerosene is safer than gasoline to have in storage and to handle. Cloud point measures the temperature at which wax crystals begin to precipitate from solution; the name comes from the fact that the liquid takes on a cloudy appearance at this point. Operating at or below the cloud point is -15 °C or lower, so that in most cold-weather circumstances there would be little problem in handling kerosene.

# 15.1.2 Jet fuel

Rockets, probably first developed in ancient China, differ from jets in that the rocket carries both a fuel and its oxidizer. About a century ago the idea of using atmospheric air as the oxidizer in a rocket-like device was developed, giving rise to the concept of the jet engine. In the airplane flying at high speed, air can be taken into the engine via an



Figure 15.1 Air Commodore Sir Frank Whittle, one of the principal inventors and developers of the aviation gas turbine, or turbojet, engine.

intake nozzle or duct. The hot, expanded combustion gases exit through a nozzle at the rear of the engine to provide the thrust. In principle, an engine of this kind, called a ramjet, could be built with no moving parts. Unfortunately, such a simple device comes with a major problem: the air needed for combustion is brought in through a duct *when the airplane is running at high speed*, so there is no way to develop thrust for take-off! And, there would be very little thrust at low-speed operation.

Engineers in Britain and Germany worked on this problem in the 1920s and 30s, though much of the credit for developing the practical jet engine for aviation goes to Sir Frank Whittle, see Figure 15.1 [A].

Whittle and his contemporaries on the Continent recognized that the problems with the ramjet could be overcome by providing a compressor to collect and compress the air needed for combustion. A turbine powered by the hot combustion products provides the mechanical work to operate the compressor. The "package" of compressor, combustion chamber(s), turbine, and shaft connecting turbine and compressor comprise a turbojet engine, illustrated in Figure 15.2. The turbojet in this form is still often used as the engine for military aircraft.

Several variants of the basic turbojet have been developed. Most large, long-range civilian passenger aircraft use a fan jet engine, also called a bypass jet engine or turbofan engine. A large fan mounted in front of the compressor helps to accumulate air for the compressor, and also helps much of the air to bypass the combustors and be added to the exhaust. Fan jet aircraft usually do not attain the high speeds of the simpler turbojets, but achieve better fuel economy, an important consideration for long-distance travel. A second variant, the turboprop or prop-jet engine, uses the mechanical work of the turbine to turn a propeller. In such engines, most of the thrust is provided by the propeller, and only a small portion is due to the jet exhaust. Turboprop engines are often used on short-haul aircraft, as in commuter flights, for example. When all of the thrust is generated by the shaft and none from exhaust, the engine is called a turboshaft. Such engines find applications where a jet exhaust would be undesirable or downright dangerous, as in helicopters, hovercraft, and some kinds of military armored vehicles.

Gas turbine engines can be designed to operate on a wide variety of fuels, including natural gas, gasoline, and ash-free coal [B]. However, the engines used in aviation,

Property	Numerical value	Maximum or minimum
Acidity, mg KOH/g	0.015	maximum
Aromatics, vol. %	25.0	maximum
Density at 15 °C, $kg/m^3$	775.0-840.0	
Distillation		
10% recovery	205 °C	
Final boiling point	300 °C	
Flash point	38 °C	minimum
Freezing point	−47 °C	maximum
Kinematic viscosity at -20 °C, cSt	8.0	maximum
Naphthalenes, vol.%	3.0	maximum
Smoke point, mm	19	minimum
Specific energy, MJ/kg	42.80	minimum
Sulfur, wt.%	0.30	maximum

 Table 15.1 Principal specifications of commercial Jet A-1 fuel.

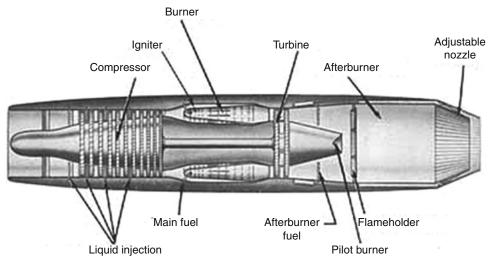


Figure 15.2 A turbojet engine. The key components are the compressor, the burner cans, and the turbine.

commonly called jet engines, operate on a carefully refined derivative of kerosene. Jet fuel is sometimes referred to as aviation gas turbine fuel, or as aviation kerosene. Numerous grades of jet fuel are produced, intended for various purposes. The most common are Jet-A and the closely related Jet A-1, widely used in civilian aviation. Table 15.1 summarizes some of the principal specifications of Jet A-1.

The principal distinction between Jet A-1, commonly used for international flights, and Jet A, used mainly for domestic flights in the United States, is that Jet A has a higher allowable pour point, -40 °C instead of -47 °C.

Many of these properties, and the reasons they are of concern, have been introduced in Chapter 14. Aromatics are precursors to soot formation. Soot can be an air-pollution problem near airports. In military aircraft, soot emissions provide a "signature" that could allow tracking the aircraft by anti-aircraft guns or missiles. Formation of soot in the engine also alters the radiative heat transfer processes. Excessive heating leads to premature degradation or failure of engine components. An indication of the sooting tendency of a fuel can be obtained from the smoke point. This property is measured in a standardized lamp, and is reported as how high a flame can be maintained before smoking or sooting is observed [C]. The higher the smoke point, the lower the tendency to produce soot. Alkanes, especially linear alkanes, tend to have high smoke points, whereas aromatics and cycloalkanes have much lower values. Sulfur, a concern because of odor, corrosion, and SOx emissions, nevertheless provides a level of lubricity for fuel pumps, when present at the 100–500 ppm level.

Jet fuel needs to remain liquid, and of viscosity low enough to be pumpable, under any anticipated operating conditions of the aircraft. At high altitudes, e.g. 10–12 km, the external air temperature is very low, perhaps -55 °C; the fuel must remain liquid down to about -45 to -50 °C in the aircraft fuel tanks. Also, fuel viscosity relates to its ability to atomize, producing fine droplets that will evaporate quickly and form the desired fuel–air mixture. The viscosity specification is normally the kinematic viscosity. Absolute, or dynamic, viscosity is the constant of proportionality between shear stress and shear rate. Kinematic viscosity is obtained by dividing absolute viscosity by the density of the fluid; doing so removes the effect of force. Kinematic viscosity has SI units of m<sup>2</sup>/s, an impractically large unit for liquids of interest in fuel chemistry. Kinematic viscosity is still commonly reported in units of Stokes, or centistokes, with 1 cSt being 10<sup>-6</sup> m<sup>2</sup>/s. (The viscosity of water at 20 °C is 1 cSt.)

The importance of volatility and distillation range comes in part from the need for the fuel to remain liquid at low external pressures during high altitude flight, e.g. pressures of 10–100 kPa. Low-boiling components can vaporize at low pressures [D]. High-boiling components can freeze at the low temperatures of high-altitude flight. In addition, a high degree of volatility helps the fuel to vaporize and mix well with the combustion air.

Density of jet fuel has two requirements that unfortunately directly counteract each other. The amount of fuel that can be loaded onto an airplane is limited by the volume of the fuel tanks. Therefore a low-density fuel is ideal, because less mass is added to the airplane by the fuel; less mass then has to be lifted off the ground and carried along on the flight. However, what ultimately propels an airplane is energy, so the more energy, as megajoules per mass of fuel, loaded, the better. Therefore, a high-density fuel is ideal, because it has a higher volumetric energy density.

Oxidation stability is of concern for long-term storage of fuel. Exposure of fuel to oxygen (air) can result in formation of gums via oligomerization of alkenes in the fuel. Gum formation begins with formation of peroxides from oxygen attack on alkenes. Gums can block filters, sensors, and meters in the fuel system. Peroxides can attack seals, gaskets, and tubing made from polymers. Anti-oxidant additives, such as 4-*tert*-butyl-2-methylphenol, are used to shut down, or at least slow down, this oxidative degradation.

Jet fuel has a secondary function, which is to act as a heat sink to provide cooling for such materials as hydraulic fluids and lubricating oils. The fuel should not degrade from exposure to high temperatures as it performs this duty. An approach to characterizing the thermal stability of jet fuels is the jet fuel thermal oxidation tester (JFTOT). As a



**Figure 15.3** Rudolf Diesel, inventor of the engine that dominates most applications other than aviation. It is the only engine using the only fuel named for the inventor.

fuel degrades because of excess heating, it produces carbonaceous deposits on hot metal surfaces. Formation of such deposits in the JFTOT and their accumulation on a filter causes a pressure drop across the filter. A typical test procedure involves passing a sample through a tube heated to 260 °C for 150 minutes at 3.45 MPa. The tube outlet contains the filter. For Jet A and A-1, the pressure drop must not exceed 3.33 kPa.

Though fuel density poses a dilemma, there appears to be increasing interest in fuels of high volumetric energy density, especially when such fuels could also provide excellent heat-sink capabilities. In this context, *trans*-decalin has much to offer: volumetric energy density higher than paraffinic fuels, thermal stability well above the JFTOT limits, and good low-temperature properties. Other materials have been investigated, and some even find some application for specialized aircraft or missiles. As an example, cyclopentadiene dimerizes in a Diels–Alder reaction, one molecule being the diene and the other the dienophile:



Hydrogenation of the dimer leads to two possible isomers: *exo-* and *endo-*tetrahydrobicyclopentadiene. The *exo-* isomer is used as JP-10 jet fuel; this specialty jet fuel is used in, e.g. aircraft-launched missiles. Two points are noteworthy: first, JP-10 is one of the very few hydrocarbon fuels that is a pure compound, rather than a mixture of tens to thousands of compounds; second, its formation via the coupling of cyclopentadiene represents easily the most important application of the Diels–Alder reaction in fuel chemistry.

#### 15.1.3 Diesel fuel

The operating cycle of the engine developed by Rudolf Diesel (Figure 15.3) [E] is somewhat similar to, but not identical with, the Otto cycle. Beginning with the intake stroke, air is drawn into the cylinder as the piston moves downward. In the compression

stroke, the rising piston compresses the air in the cylinder. A Diesel engine has a much higher compression ratio than an Otto engine; 15:1 up to 25:1, compared to 8:1 to 11:1 in most modern Otto-cycle engines. The higher the compression ratio, the higher the pressure in the cylinder, and the hotter the air. An instant before the piston reaches the top of its stroke – i.e. top dead center – fuel is injected into the hot, high-pressure gas in the cylinder. The fuel ignites by autoignition. A Diesel engine has no spark plugs. Energy liberated from the combustion of the fuel is converted to mechanical energy as it pushes the piston downward. Finally, in the exhaust stroke, the piston moves upward and pushes the products of combustion out of the cylinder into the exhaust manifold.

Autoignition also occurs in the context of the engine knock problem in spark-ignition engines (Chapter 14). Autoignition in a diesel engine is not the same thing as knocking in a spark-ignition engine. In a gasoline engine, autoignition, if it occurs at all, takes place in a small and localized region of the cylinder. The energy released from autoignition of gasoline represents only a small fraction of the total energy released from the particular amount of gasoline in the cylinder. On the other hand, operation of the diesel engine depends on the ability of the fuel to undergo autoignition. The fuel-air mixture is heterogeneous, since it is likely that not all of the fuel has had time to evaporate. Autoignition might occur at several locations within the cylinder. Any autoignition process puts significant mechanical stresses on the engine, but the diesel engine is designed to accommodate these, whereas a gasoline engine is not. Further, it might be expected that a fuel with good autoignition quality for diesel service would be the opposite, in composition, to a good gasoline, where autoignition is not desired. Linear alkanes are desirable in diesel fuel, whereas aromatics and branched-chain alkanes are not. Ideally it might be useful to adopt a sort of inverse octane scale to characterize diesel fuel. However, diesel fuel has a much higher boiling range than gasoline, so heptane and 2,2,4-trimethylpentane would not be present in any significant amount in diesel fuel. For rating diesel fuel, a different, but somewhat analogous, scale is created. Since *n*-alkanes are desirable in diesel fuel, hexadecane,  $C_{16}H_{34}$ , becomes the preferred component, arbitrarily assigned a value of 100. The aromatic compound 1-methylnaphthalene is assigned a value of 0. The rating system takes the name cetane number, from the trivial name for hexadecane. Cetane number (see Table 15.2) is equivalent to the percentage of cetane in a cetane: 1-methylnaphthalene blend that gives the same engine performance under standardized test conditions. A good-quality diesel fuel for operation in an automobile or light truck engine would have a cetane number of  $\approx$ 50. Difficulty in obtaining large quantities of pure 1-methylnaphthalene (in particular, free of the 2-methylnaphthalene isomer) has led to adoption of an alternative reference standard, 2,2,4,4,6,8,8-heptamethylnonane. Since branched-chain alkanes are also undesirable in diesel fuel, this compound is assigned a cetane number of 15.

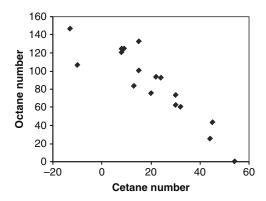
As a rule, for compounds of the same number of carbon atoms, cetane number drops in the order *n*-alkane > alkene > cycloalkane > alkylaromatic. Among *n*-alkanes, cetane number decreases as the number of carbon atoms drops.

Since linear alkanes are desirable components of diesel fuel but undesirable in gasoline, there is an approximate relationship between octane and cetane numbers for various compounds, when both are known. Figure 15.4 shows this.

Diesel engines can be designed to run on a wide variety of fuels. (This does not imply that the *same engine* can utilize many different kinds of fuel, but rather that, with appropriate design, different engines can handle different fuels.) One of Diesel's early

Compound	Cetane npound number Compound		Cetane number	
C <sub>4</sub> compounds		C <sub>10</sub> compounds		
<i>n</i> -Butane	22	Tetralin	13	
C <sub>5</sub> compounds		trans-Decalin	48	
<i>n</i> -Pentane	30	1-Decene	56	
$C_6$ compounds		2,2-Dimethyloctane	59	
Benzene	-10	<i>n</i> -Decane	76	
Cyclohexane	13	C <sub>12</sub> compounds		
2,2-Dimethylbutane	24	2,3,4,5,6-Pentamethylheptane	9	
2-Methylpentane	30	<i>n</i> -Hexylbenzene	26	
<i>n</i> -Hexane	44	1-Dodecene	71	
C7 compounds		<i>n</i> -Dodecane	82	
Toluene	9	C <sub>16</sub> compounds		
Methylcyclohexane	20	2,2,4,4,6,8,8-Heptamethylnonane	15	
1-Heptene	32	4-(n-Octyl)-1,2-dimethylbenzene	20	
<i>n</i> -Heptane	54	7,8=Dimethyltetradecane	40	
C <sub>8</sub> compounds		4-Butyl-4-dedecene	45	
<i>p</i> -Xylene	-13	1-Hexadecene	87	
o-Xylene	8	<i>n</i> -Hexadecane	100	
Ethylbenzene	8	C <sub>20</sub> compounds		
2,2,4-Trimethylpentane	15	3,6-Dimethyl-3-naphthyloctane	18	
Ethylcyclohexane	45	2-Phenyltetradecane	49	
<i>n</i> -Octane	64	2-Cyclohexyltetradecane	57	
C <sub>9</sub> compounds		9,10-Dimethyloctadecane	60	
Isopropylbenzene	15	<i>n</i> -Tetradecylbenzene	72	
<i>n</i> -Nonane	73	<i>n</i> -Eicosane	110	

Table 15.2 Cetane numbers of selected compounds.



**Figure 15.4** Because of the different principles of the Otto and Diesel cycles, there should be an approximately inverse relationship between octane and cetane numbers. That is illustrated here with data for pure compounds.

engine developments was intended to run on coal tar. Diesel's demonstration engine for the 1900 Paris Exposition operated on peanut oil. Diesel engines have successfully operated on gaseous fuels such as natural gas and dimethyl ether. However, most Diesel engines in use nowadays are designed to operate on the petroleum distillate

	Numerical value (maximum or minimum)				
Property	Europe, Class A	United States, 1-D	United States, 2-D		
Aromatics, vol. %	_	35 (max.)	35 (max.)		
Cetane number	49	40	40		
Cold filter plugging point, °C	5 (max.)	_	-		
Density, kg/l	0.820 (min.)	_	_		
	0.860 (max.)	_	_		
Distillation points, °C					
<65% distilled	250	_	_		
>85% distilled	350				
90% distilled	_	288 (min.)	282 (min.)		
	_	-	338 (max.)		
>95% distilled	370	_	-		
Flash point, °C	55 (min.)	38	52		
Kinematic viscosity at 40 °C, mm <sup>2</sup> /s	2.0 (min.)	1.3 (min.)	1.9 (min.)		
· · ·	4.5 (max.)	2.4 (max)	4.1 (max.)		
Sulfur, wt. %	0.05 (max.)	0.05 (max.)	0.05 (max.)		

**Table 15.3** Examples of diesel fuel specifications. A dash indicates that the property is not part of the specification. Cloud point specifications vary by region.

called diesel fuel or diesel oil. Because of the increasing interest worldwide in biodiesel, and in diesel fuel made via the Fischer–Tropsch process (Chapter 21) the term "petrodiesel" is sometimes used to denote the fuel made from petroleum. This type of fuel exists in a number of grades (Table 15.3), which vary in quality according to the engine or according to the use to which they will be put. As examples, grade 1-D is intended for engines that have frequent speed and load changes, such as might be typical of cars and light trucks. Grade 2-D is intended for "heavy mobile service," typical of many of the engines in industrial use.

Distillation behavior provides insights into combustion performance. Too large a proportion of high-boiling constituents indicates that atomization of the fuel after injection into the cylinder could be difficult; consequently the smooth, steady combustion of fuel during the power stroke may be impeded. Since high-boiling components are often rich in aromatic soot precursors and may contain sulfur in hard-to-treat heterocyclic compounds, a large proportion of high-boiling compounds may indicate problems with engine emissions. Flash point relates to fuel safety for storage, handling, and distribution, since the higher the flash point, the lower the likelihood that the fuel will ignite accidentally in the presence of a spark or flame.

Viscosity is important in satisfactory operation of the fuel injection pump and fuel injectors. Too high a viscosity results in increased pumping losses and reduced injection pressure. The latter problem then cascades into reduced fuel atomization and from there to problems with the combustion process. Too low a viscosity could result in leakage at the pump or, in the worst case, having the fuel pump seize. Viscosity of any liquid increases as temperature drops. The nature of the viscosity–temperature relationship of the fuel has particular importance for operation of diesel engines in cold weather.

Cloud-point specifications, not listed in Table 15.3, vary from one region to another, depending on the prevailing climate, and in some cases vary with season or month. At temperatures below the cloud point, more and more wax crystallizes. A point can be reached at which the wax crystals cannot pass through fuel filters. This causes partial or complete blockage of the fuel filters, which can then slow fuel flow or even stop it altogether. Continued cooling results in the increasing mass of crystals "locking up" any remaining liquid phase, preventing the liquid from flowing at all. At this temperature, a beaker containing a sample of this fuel can be tilted  $90^{\circ}$  and the sample will still not flow out of it. This behavior defines the pour point of the fuel. Similar to cloud-point specifications, requirements for pour point vary widely around the world, from +4 °C in India to -40 °C in Scandinavia. In modern vehicles the fuel system has a filter, with pore sizes in the micrometer range, upstream of the fuel injection pump. This filter can become clogged at low temperatures when waxes crystallize from the fuel. The cold filter plugging point (CFPP) is the temperature at which 20 ml of fuel will stop flowing in less than 60 seconds through a standardized filtration apparatus. CFPP requirements also vary regionally within Europe, but typically range from -10 to -30 °C. A straightforward way of reducing the cloud point is to reduce the distillation cut points. Reducing the final distillation temperature removes some of the highmolecular-weight alkanes that would contribute to wax crystallization. Reducing the initial temperature retains in the liquid some light compounds that could act as solvents to help keep crystals in solution.

Operation of a diesel engine is not simply a matter of injecting the fuel and air together, because the mixture could burn in an uncontrolled fashion analogous to knocking in a spark-ignition engine. In that case, the best that could be hoped for is to have the engine run smoothly at one speed and at one load [F]. For automobile and light truck applications, the use of a fuel injector overcomes this problem. Air is admitted to the cylinder and heated by the compression work of the engine. Fuel is then injected into the heated air, producing a mixture of suspended fuel droplets of various sizes. At various places within this heterogeneous mixture the air/fuel ratio is locally correct, and enough fuel will have vaporized to insure ignition. Fuel injection continues for most of the power stroke in the cylinder. Over wide ranges of air/fuel ratio there are some locations in the cylinder at which the conditions needed to obtain ignition prevail. Reliable ignition and smooth performance can be obtained over a wide range of engine loads.

Evaporation of fuel, once injected into heated air in the cylinder, is crucial to maintain good mixing of the fuel with air. Furthermore, fuel droplets must partially vaporize before combustion can start. The heat required for vaporization is a portion of the heat released from the combustion reactions. Volatility is important, but because vaporization is driven in part by the heated air in the cylinder, diesel fuel need not be as inherently volatile as gasoline. "Atomizing" the fuel to very fine droplets also promotes evaporation by achieving a high surface-to-volume ratio in the droplets.

Density is important for several reasons. The fuel pump and injectors deliver a specified volume of fuel to the engine, but combustion performance once in the engine depends on fuel-to-air stoichiometry, which is based on mass. The property relating volume to mass is density. High density provides greater vehicle range per volume of fuel, expressed as the volumetric energy density. Gasoline has a superior calorific value on a mass basis (48 MJ/kg, compared to 45 MJ/kg for diesel fuel). However, diesel has a

	No. 1	No. 2	No. 4	No. 5	No. 6
API gravity, degrees	40	32	21	17	12
Ash, wt.%	trace	trace	0.02	0.05	0.08
Calorific value, MJ/l	38.2	39.3	40.7	41.2	41.8
Color	light	amber	black	black	black
Pour point, °C	<-18	<-18	-12	-1	18
Sulfur, wt.%	0.1	0.4 - 0.7	0.4-1.5	$\leq 2.0$	$\leq 2.8$
Viscosity, mPa·s	1.6	2.7	15	$\frac{-}{50}$	360

**Table 15.4** Principal characteristics of distillate and residual fuel oils in the classification used in the United States.

good bit higher density, 0.88 kg/l vs. 0.74 kg/l for gasoline. As a result, when the fuels are compared in terms of calorific value per unit volume, diesel is superior: 39 MJ/l vs. 35 MJ/l for gasoline.

Ignition delay of a diesel fuel is the time lapse between the instant at which the first fuel droplets enter the cylinder and the instant at which combustion begins. Ignition delay has both a physical and a chemical aspect. The physical part is the time interval between the fuel coming into the cylinder from the injector and the establishment of a fuel–air mixture ready for autoignition. The chemical portion includes those processes that result in the actual autoignition of the fuel, once the appropriate fuel–air mixture has been created. The chemical portion depends on the temperature and pressure in the cylinder, as well as on the chemical characteristics of the fuel, as expressed, e.g. in terms of cetane number.

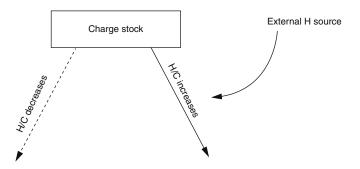
Improvements in ignition quality of diesel fuels can be obtained by addition of ignition accelerators, sometimes also called pro-knocks, cetane improvers, or cetane enhancers. Several classes of compound function as cetane improvers, of which the most popular class is the alkyl nitrates. Examples include ethylhexyl nitrate and pentyl nitrate (also called amyl nitrate). Their ability to improve cetane number depends on the quality of the original fuel. With 2-ethylhexyl nitrate, for example, addition of 0.20% by volume to a fuel initially of 25 cetane raises the cetane number to  $\approx$ 30. The same amount added to a 45-cetane fuel will increase the cetane number to 53. Addition of 2 volume percent amyl nitrate can enhance the cetane number of a diesel fuel by  $\approx$ 20 points.

## 15.1.4 Fuel oils

Fuel oils serve many purposes. They can be burned: for space heating, including domestic heat; for providing process heat in chemical or metallurgical processes; or to raise steam, either for operating engines, as in ships, or for steam turbines in electric power plants. Fuel oils broadly divide into two categories, distillate and residual oils. Distillate oils are distillation products, while the residual oils derive from the residuum.

In the United States, fuel oils are graded on the basis of viscosity. The classification uses a numbering system, illustrated in Table 15.4.

No. 1 fuel oil is comparable to kerosene and to 1-D diesel fuel. Though these three materials have different specifications (e.g. there is no cetane specification for fuel oil), they could be considered nearly interchangeable. The same is true for No. 2 fuel oil, and



**Figure 15.5** Providing an external source of hydrogen changes the rules of hydrogen distribution. In such a case it is possible to make products having atomic H/C higher than that of the feedstock, without necessarily producing carbon-rich products at the same time.

2-D diesel. The other three oils are residual oils. No. 5 and 6 oils, sometimes called bunker oils, have to be heated to be pumped through fuel lines and burner nozzles in combustion equipment. They are dominated by very large molecules, generally with more than 20 carbon atoms. In some cases their pour points can exceed 20  $^{\circ}$ C.

# 15.2 Hydroprocessing

The family of operations collectively known as hydroprocessing involves treatment of selected streams with hydrogen. Hydroprocessing is done for various purposes. It includes processes designed to treat the feed to remove impurities, such as potential catalyst poisons, before further reaction; to improve the characteristics of a product to meet market or performance specifications, such as removal of sulfur compounds; and cracking large molecules into lower-boiling materials. Virtually all of the fossil-fuel reaction processes discussed to this point have taken place with the constraint that hydrogen moved among molecules during these reactions is limited to internal hydrogen, i.e. hydrogen originally present in the system. The consequence is that formation of hydrogen-rich products is inevitably accompanied by carbon-rich products. Since usually (not always) the hydrogen-rich light products have the greater value, the accompanying carbon-rich products – polycyclic aromatic compounds, tars, soots, or cokes – often represent problems. Supplying an external source of hydrogen changes the rules. Having abundant hydrogen in the system can close off, or diminish, the formation of the carbon-rich products and can enhance the yield of the hydrogen-rich, light products such as gasoline and jet fuel. Figure 15.5 schematically represents this new situation.

This is not to imply that utilization of the external source of hydrogen is necessarily easy. Sometimes hydroprocessing requires severe reaction conditions, including high partial pressures of hydrogen, and special catalysts.

The broad field of hydroprocessing encompasses several kinds of process. Hydrogenation has as its primary purpose increasing the H/C ratio of the feed, such as by saturating aromatic compounds or alkenes. Doing so helps to stabilize middle distillate fuels by minimizing gum and sediment formation, and can help shift the distillation curve to lighter products. Hydrocracking decreases the molecular weight, and therefore the boiling point, by reducing molecular size. Hydrotreating removes heteroatoms, particularly nitrogen and sulfur, and sometimes metals. Frequently a process run to achieve a particular outcome, e.g. hydrodesulfurization, is accompanied by other reactions, such as hydrogenation.

## 15.2.1 Hydrodesulfurization

Concerns about the impact of sulfur oxide emissions on air quality result in a continual worldwide focus on reducing the sulfur concentration in fuels. Direct exposure to sulfur oxides in the atmosphere results in irritation or injury to sensitive tissues in the eyes and respiratory tract. Acid precipitation causes a variety of ecological problems, including acidification of natural waterways and consequent destruction of aquatic life, crop damage due to leaching of plant nutrients from the soil, and even direct attack on sensitive plant tissues.

Strategies for dealing with the sulfur content of fuels and reducing emissions of sulfur oxides fall into two broad categories: pre-combustion and post-combustion. Precombustion strategies reduce or eliminate the sulfur content before the fuel is burned. Post-combustion strategies deal with sulfur oxides once they have been formed in combustion. The most successful post-combustion strategy controls sulfur oxide emissions in devices called scrubbers, which react the sulfur oxides with an aqueous slurry of calcium hydroxide or calcium carbonate:

$$Ca(OH)_2 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + H_2O_2$$

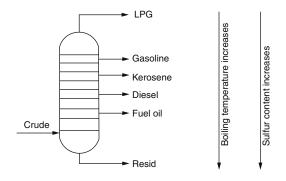
While applicable in principle to any sulfur-containing fuel, use of scrubbers has mainly been applied to coal-fired power plants. Scrubbers work very well. They are suitable for power plants because they do not move around (i.e. are so-called stationary sources), and power plants are usually so large, consuming in the order of  $10^4$  tonnes/day of coal, that significant economies of scale can be achieved. Scrubbers would be impractical on mobile sources – cars, trucks, and locomotives. Pre-combustion strategies make much more sense. Examples of pre-combustion strategies include sweetening of sour gas (Chapter 10), and removing sulfur-containing minerals from coal. The principal sulfur-containing mineral in coal, pyrite, has a much higher density than the carbonaceous portion of coal, so its concentration can be reduced by processes that rely on density differences. With petroleum products the situation is more difficult, because sulfur is chemically incorporated in various organic molecules in the fuel itself, not easy to remove by simple differences in physical properties or absorption [G].

Hydrodesulfurization (HDS) provides a route to reducing the sulfur content in liquid fuels by reaction with hydrogen:

$$\mathbf{R}\!-\!\mathbf{S}\!-\!\mathbf{R}'+2\,\mathbf{H}_2\rightarrow\mathbf{R}\!-\!\mathbf{H}+\mathbf{R}'\!-\!\mathbf{H}+\mathbf{H}_2\mathbf{S}.$$

Some hydrodesulfurization might occur as one process amongst many in catalytic reforming. Hydrodesulfurization is often run in a separate reactor upstream of other refinery operations.

Sulfur is more of a problem with diesel fuel than with gasoline, even for fuels distilled from the same oil. The chemistry is complicated by the fact that sulfur can occur in a number of different functional groups. As examples, the effect of sulfur on boiling temperatures can be illustrated by considering two sulfur groups:



**Figure 15.6** Because sulfur-containing compounds boil at temperatures higher than the related hydrocarbon compounds, a distillation tends to concentrate sulfur into the higher-boiling fractions.

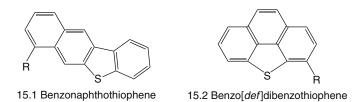
sulfides, which are the sulfur analog of ethers; and thiols or mercaptans, the sulfur analog of alcohols. Heptane,  $C_7H_{16}$ , has a molecular weight of 100 Da and a boiling point of 98 °C. If, conceptually, the central methylene group in heptane is replaced by a sulfur atom (entirely glossing over how this might be done in the laboratory) the resulting compound, dipropyl sulfide,  $C_3H_7SC_3H_7$ , has a molecular weight of 118 Da and boiling point of 142 °C. The increased molecular mass in dipropyl sulfide compared to heptane would require more thermal energy to be added to the liquid to move molecules from the liquid to the vapor state. But, this is not the whole story. Octane, with a molecular weight of 114 Da, about as close as a hydrocarbon can come in molecular weight to dipropyl sulfide, boils at only 125 °C. Some additional effect, besides molecular mass, must help account for the increased boiling point of dipropyl sulfide relative to heptane. This could derive from the ability of a sulfur atom to sustain a dipole for longer than the transitory dipoles associated with London-force interactions, possibly because of the availability of *d*-orbitals on the sulfur atom.

1-Hexanethiol,  $C_6H_{13}SH$ , an isomer of dipropyl sulfide and therefore of the same molecular mass, boils at a temperature even higher, 150 °C. In this compound, the thiol group introduces a permanent dipole into the molecule. This dipole is not as strong as in the corresponding alcohols, but still increases intermolecular interactions.

A good rule of thumb is that the boiling points of organosulfur compounds are higher – sometimes a good bit higher as with heptane and dipropyl sulfide – than those of structurally similar hydrocarbons. This affects the distribution of sulfur during distillation. While the objective of distillation is to achieve a fractionation based on boiling temperature ranges, because of the differences in boiling points of sulfur compounds relative to their hydrocarbon analogs, a fractionation based on sulfur content also occurs (Figure 15.6). For a given oil fed to the distillation tower, the sulfur content of the distillation cuts increases as boiling temperature increases.

Generally, fuels in the gasoline and naphtha range contain thiols, sulfides, disulfides, and alkylated derivatives of thiophene. Middle distillate fuels in the jet fuel range contain heterocyclic compounds such as benzothiophene and dibenzothiophenes. Diesel fuel can contain such compounds as dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene. Heavy fuel oils contain even larger

compounds, heterocycles with three or more fused rings, such as benzonaphthothiophenes (15.1): and benzo[*def*]dibenzothiophenes (15.2):



(where in both cases there may be more than one alkyl substituent, and maybe on ring positions other than the one illustrated).

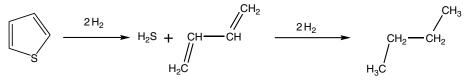
Europe and the United States have increasingly strict environmental regulations concerning the allowable sulfur content in diesel fuel. Additional regulations will, without doubt, be coming in the future. Tightening of standards on allowable sulfur content of diesel fuel poses problems for refiners. Hydrogen is expensive; the greater the degree of desulfurization required, the more costly the process. And, the law of diminishing returns sets in [H]. Often, to progress from 90% to 99% removal of an impurity (e.g. sulfur) takes as much work as going from 0 to 90%; and going from 99 to 99.9% is as hard as the step from 90 to 99%. But, this field poses excellent research and development opportunities for developing new, efficient, and cost-effective approaches to "deep desulfurization."

Narrowly defined, the outcome of hydrodesulfurization should be a hydrogenolysis of a C–S bond. With a sulfide, for example, the reaction would be

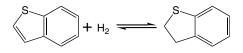
$$\mathbf{R} - \mathbf{S} - \mathbf{R}' + 2\mathbf{H}_2 \rightarrow \mathbf{R} - \mathbf{H} + \mathbf{H} - \mathbf{R}' + \mathbf{H}_2 \mathbf{S}.$$

However, hydrodenitrogenation, hydrogenation of aromatics or alkenes, and some degree of hydrocracking often accompany HDS.

The reaction of thiophene illustrates HDS chemistry:



Reaction begins with C–S bond cleavage to form 1,3-butadiene, which subsequently undergoes hydrogenation. C–S bond cleavage does not require reduction of the aromatic ring as a necessary first step [I]. For more complex molecules, e.g. benzothiophene, hydrogenation may compete with hydrodesulfurization:



Both benzothiophene and 2,3-dihydrobenzothiophene could then undergo desulfurization. However, reduction of an aromatic ring is not necessary for hydrodesulfurization to take place. For example, dibenzothiophene reacts to give biphenyl. The many sulfur-containing functional groups each have a characteristic reactivity in HDS. Generally, reactivity has the order thiols > disulfides > sulfides > thiophenes > benzothiophenes > dibenzothiophenes > larger aromatic heterocycles (e.g. benzonaphthothiophenes). The boiling points of these compounds would probably increase in the same order, and this leads to the difficult situation that not only do higher-boiling distillation cuts contain more sulfur, but they also tend to be less reactive in HDS. Within a single compound class, low molecular weight compounds react more readily than those of higher molecular weight. The problem comes from the fact that sulfur compounds tend to be at higher concentrations in the higherboiling fractions, making these materials more likely to require HDS to meet specifications; yet the compounds in these fractions are less reactive in HDS. Thus the higher boiling fractions are at the same time more likely to require HDS and harder to desulfurize.

In principle, almost any effective hydrogenation catalyst could be used for HDS, but with one important consideration. Sulfur is an effective poison for many metallic catalysts, such as platinum. To avoid this problem, HDS often uses as catalysts transition metal sulfides, or transition metal oxides that have been "pre-sulfided" before being used in HDS. Molybdenum is frequently used to formulate HDS catalysts; tungsten is also effective. Especially useful catalysts employ one of these metals, usually molybdenum, in combination with cobalt or nickel as a promoter. Neither cobalt nor nickel by itself works well in HDS, but they act as promoters when in the presence of molybdenum or tungsten. Because HDS catalysts are designed to be sulfur-tolerant, poisoning by sulfur compounds is not an issue. Coking, though, can occur on an HDS catalyst, by oligomerization or polymerization of large aromatic molecules. Running the HDS unit at high hydrogen pressures (up to 20 MPa, though 1–5 MPa is more common) helps suppress coke formation.

During HDS, hydrogen, hydrogen sulfide, and the organosulfur reactant all adsorb on the catalyst surface. Hydrogen undergoes dissociative chemisorption to form hydrogen atoms. The active metal, e.g. molybdenum, contributes electrons in processes such as

$$Mo^{+3} \rightarrow Mo^{+4} + e^{-}$$
.

Molybdenum compounds may be good in this application because they easily shuttle back and forth between different oxidation states, e.g.  $Mo^{+3}$  and  $Mo^{+4}$ , which might in turn aid in shuttling electrons between the oxidation and reduction reactions. Using thiophene as an example of the organosulfur compound, the reaction occurs as

$$C_4H_6S + 2H + 2e^- \rightarrow CH_2 = CHCH = CH_2 + S^{-2}$$

Sulfide reacts with adsorbed hydrogen as

$$S^{-2} + 2H \rightarrow H_2S + 2e^-$$

Overall, HDS includes both electron transfer and hydrogen transfer processes.

It is likely that the catalyst promoter, usually cobalt, acts by creating defect sites on the catalyst surface. Normally the expected sulfide of cobalt would be CoS. However, in the HDS catalyst a non-stoichiometric sulfide, such as  $Co_8S_9$ , could be present and facilitate formation of sulfur vacancies on the catalyst surface. Incorporation of the

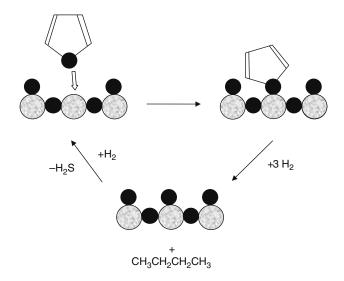
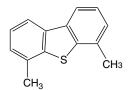


Figure 15.7 During hydrodesulfurization, sulfur atoms in the feedstock interact with sulfur vacancies on the surface of the catalyst.

sulfur atom in the molecule undergoing HDS into a vacant site on the catalyst surface (e.g. Figure 15.7) can be an important step in the mechanism of HDS.

The relative reaction rates for compounds during the HDS of diesel and similar middle distillate fuels are thiophene > benzothiophene > dibenzothiophene > 4-methyldibenzothiophene > 4,6-dimethyldibenzothiophene. So-called deep desulfurization of middle distillate fuels requires removal of such heavy compounds as 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (15.3).



15.3 4,6 Dimethyldibenzothiophene

These compounds are extremely difficult to deal with because the methyl groups prevent the sulfur atom from occupying the sulfur vacancies on the catalyst surface. Dibenzothiophene derivatives with methyl substituents in positions other than the 4and 6-positions are much easier to react.

Figure 15.8 is a simplified flow diagram for an HDS operation.

HDS process conditions depend on the feedstock. For light- or middle-distillate fuels, HDS would run at 300–400 °C and a linear hourly space velocity (LHSV) of 2–10 hr<sup>-1</sup>. Hydrogen is added in an amount of  $350 \text{ m}^3/\text{m}^3$ . Hydrogen consumption is of the order of  $50-350 \text{ m}^3/\text{m}^3$ . Good catalyst lifetimes can be expected, up to ten years in the best cases. In comparison, HDS of resids is run at 340–425 °C and LHSVs of 0.2–1 hr<sup>-1</sup>. With these feeds, hydrogen consumption can be in the range 350–1750 m<sup>3</sup>/m<sup>3</sup>, with catalyst lifetimes sometimes being less than a year. HDS of straight-run kerosene over a CoMo catalyst on alumina produces jet fuel; the same process applied to straight-run light gas oil yields

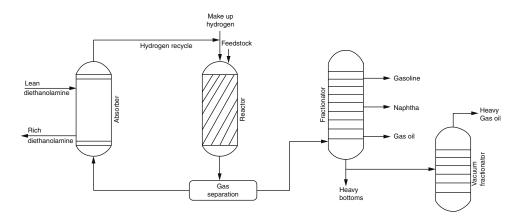


Figure 15.8 Process flow for hydrodesulfurization.

diesel fuel. Hydrogen sulfide produced during HDS must be treated to prevent its escaping to the environment, e.g. by the Claus process (Chapter 20). Briefly, a portion of the  $H_2S$  formed during HDS is burned to produce  $SO_2$ . The  $SO_2$  is then reacted with the remainder of the  $H_2S$  to form elemental sulfur:

$$2 \operatorname{H}_2 S + SO_2 \rightarrow 2 \operatorname{H}_2 O + 3 S.$$

Sulfur produced in this reaction can be sold to the chemical industry for making sulfuric acid. Since some hydrocracking accompanies HDS, about 5–15% of the feed is converted to material boiling below  $\approx$ 350 °C.

Two side reactions can accompany HDS. An HDS catalyst is often a good hydrogenation catalyst as well. Aromatic compounds in the feedstock can be fully or partially hydrogenated ("saturated"), e.g. conversion of naphthalene to tetralin or even decalin, although reaction conditions can be adjusted to avoid extensive hydrogenation. Nevertheless, some hydrogenation of aromatics almost always accompanies hydrodesulfurization. The other side reaction, hydrocracking, is discussed below.

#### 15.2.2 Hydrodenitrogenation

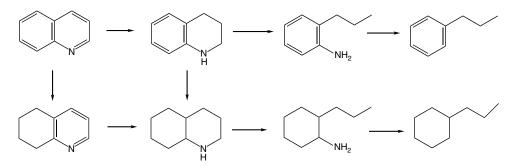
Nitrogen compounds in fuel contribute to emission of nitrogen oxides from combustion systems. Atmospheric nitrogen oxides participate in formation of acid precipitation and formation of photochemical smog. In most combustion processes, nitrogen oxides arising from nitrogen incorporated in fuel molecules, so-called fuel NO<sub>x</sub>, contribute only a small proportion to the total nitrogen oxides. Air in the combustion chamber contains 80% nitrogen, which reacts with oxygen at the high temperatures of the combustion process, e.g.

$$N_2 + O_2 \rightarrow 2 NO,$$
  
 $N_2 + 2 O_2 \rightarrow 2 NO_2$ 

This thermal  $NO_x$  usually dominates the total  $NO_x$  production. Not much gain in air quality is achieved by reducing fuel  $NO_x$ , or its precursor, nitrogen atoms in the fuel molecules. Concern about nitrogen compounds in fuels arises from the fact that many such compounds can be good Lewis bases or Brønsted bases. This chemical behavior

makes nitrogen compounds profound poisons for acidic catalysts. In addition, nitrogen compounds in lubricating oils are not stable at high temperatures, and can decompose or form polymeric solid deposits, compromising the lubricating ability of the oil.

Hydrodenitrogenation (HDN) has some similarity to HDS, in that the objective is to cleave, in this case, a C–N bond, to reduce the heteroatom concentration. A distinction in the chemistry is that, in HDN, rings need to be saturated before the nitrogen can be removed, whereas HDS of aromatic sulfur-containing heterocycles does not require complete reduction of the ring. A typical sequence of reactions in the HDN of quinoline would be



In this example, HDN of quinoline ultimately produces propylbenzene and propylcyclohexane. Various HDN processes operate over a wide range of pressure, 1-17 MPa, but all tend to be in the temperature range of 340-400 °C.

Often the same, or similar, catalysts can be used for HDS and HDN. Both oxide and sulfide catalysts can be effective. The catalysts do not need to be presulfided before use. Typical catalysts are molybdenum, or sometimes tungsten, with nickel as a promoter, on alumina support. Nickel seems to be a more effective promoter for HDN catalysts than is cobalt.

## 15.2.3 Hydrodemetallation

Hydrodemetallation (HDM) removes nickel and vanadium from refinery streams. These metals poison catalysts used for downstream processing, can accelerate corrosion of combustion systems if allowed to remain in final fuel products, and are toxic in their own right. Nickel and vanadium occur in petroleum as porphyrin complexes, surviving from the original organic matter. When metal has deposited on, e.g. a hydrocracking catalyst, it is impossible to remove. The only solution is to replace the catalyst.

## 15.2.4 Hydrofining

Hydrofining usually is run to upgrade naphthas for feed to catalytic reforming. It can also be applied to other products, such as gas oils, or even feeds as heavy as lubricating oils. Hydrofining operates at relatively mild conditions, e.g. 0.35-6 MPa, over a range of temperatures as low as 200 °C (though up to 400 °C, depending on the feed). A typical catalyst would be molybdenum oxide, with a cobalt promoter, on alumina. The process reduces sulfur content. It reduces gum-forming tendencies by saturating

alkenes. Not much reduction of aromatics is achieved (except at the most severe conditions), so little improvement in sooting tendency occurs. Suppression of coke formation, thanks to the available hydrogen, provides very long on-stream times for hydrofining catalysts before regeneration is needed.

### 15.2.5 Hydrocracking

The feed for hydrocracking is often gas oils, from resid processing or from thermal cracking or delayed coking operations (Chapter 16). These are not the same kinds of feed that normally go to the FCC unit. Hydrocracking reactions include breakdown of long-chain alkanes and removal of side chains from alkylaromatics. Hydrocracking reactions resemble those already discussed for catalytic cracking and proceed via similar mechanisms. The key difference lies in the external hydrogen available for hydrocracking. Carbocations usually convert rapidly to alkanes by further hydrogenation. The high hydrogen partial pressure prevents condensation of alkenes that would otherwise lead to coke formation. Polycyclic aromatics, also coke precursors, undergo partial hydrogenation, followed by hydrocracking into smaller, less condensed aromatic structures.

The distinction between hydrocracking and hydrotreating operations lies in the intended outcomes with respect to boiling range of the products. In hydrocracking the intent is to convert the feed, 100% if possible, to products boiling below the boiling range of the feed. In hydrotreating, a marked shift in boiling range is not the primary intent, though some shift may occur by reducing the amounts of aromatics and sulfur compounds in the feed. The primary goal of hydrotreating is improvement in quality of the feed by removing or reducing undesirable sulfur, nitrogen, alkenes, and aromatics.

Hydrocracking employs bifunctional catalysts, with a metallic component to promote hydrogenation, and an acidic support to enhance cracking. An example is nickel on a silica-alumina support. If high-sulfur feeds are used, the hydrogenation catalyst would need to be in its sulfided form, to avoid poisoning by sulfur. Resid hydrocracking is used to upgrade distillation residua to distillable products. Compared to catalytic cracking, hydrocracking produces less gas and less coke, and therefore more liquid. Hydrocracking is overall exothermic, whereas catalytic cracking is endothermic. But, because hydrocracking employs an external source of hydrogen, an expensive reagent, hydrocracking processes are more costly than catalytic cracking. Cracking usually is less extensive in hydrocracking, because the hydrogen present in the reactor helps to stabilize the primary products, making them less likely to crack further.

In hydrocracking, two adjacent carbon atoms in a molecule of feedstock adsorb on the catalyst surface (Figure 15.9). Loss of hydrogen atoms leads to strong carbon-to-catalyst bonds. Addition of H• from the catalyst stabilizes these fragments and lets them desorb from the catalyst surface as new, shorter molecules, as in Figure 15.11.

Hydrocracking typically runs at 10–20 MPa and 300–370 °C. Conversion of heavy feeds to 350<sup>-</sup> products relates to the amount of hydrogen consumed. For example, consumption of hydrogen amounting to about 1% by weight of the feed results in  $\approx$ 30% conversion of heavy oil feed to lighter materials. Conversions of 90–100% correspond to hydrogen consumptions of 5–5.5% by weight. Table 15.5 compares aspects of catalytic cracking and hydrocracking.

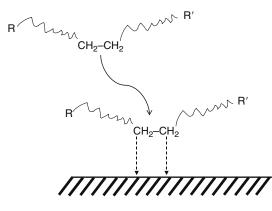
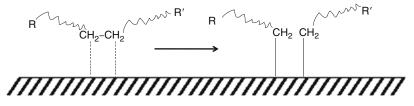


Figure 15.9 Hydrocracking begins with interaction of carbon atoms in the feedstock with the catalyst surface.



**Figure 15.10** After adsorption onto the hydrocracking catalyst, a carbon-carbon bond in the feedstock breaks.

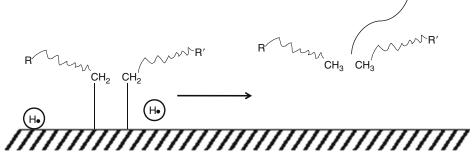
Catalytic cracking shows a higher selectivity, in that a more narrow spectrum of products results. But, in hydrocracking, alkenes do not appear in the gasoline, and coke formation is significantly lower.

Many reaction variables affect the outcome of hydrocracking. Temperature has the dominant role. As in many other reactions, a 10 °C increase can effect a near-doubling of reaction rate. Conversion increases with an increase in hydrogen partial pressure. If hydrocracking is accompanied by some hydrodenitrogenation, ammonia is also present in the reactor atmosphere. Increased ammonia partial pressure appears to decrease conversion, an effect that is outweighed by the benefit of the increased hydrogen partial pressure. That is, increased reactor pressure enhances conversion. An increase in feed rate decreases conversion, because a given amount of feed has less time in contact with the catalyst.

Hydrocracking could be applied to a material such as light vacuum gas oil, dominated by  $C_{25}$ – $C_{35}$  compounds. This material would be hydrocracked over a NiMo catalyst on alumina. The product slate includes  $C_3$  and  $C_4$  gases and, as liquids, highoctane gasoline and middle distillates, notably jet fuel and diesel. The lighter gasoline fractions, i.e. pentane and hexane isomers, have octane numbers of  $\approx$ 95–100 RON; heavier gasoline fractions of lower octane could be candidates for catalytic reforming. As mentioned above, some hydrocracking accompanies HDS or HDN. The converse is also true, i.e. hydrocracking a sulfur- or nitrogen-rich feed is accompanied by some extent of hydrodesulfurization or hydrodenitrogenation.

	Catalytic cracking	Hydrocracking
Boiling range of feed, °C	230-600	50-540
Hydrogen consumption, wt.%	0	1.5–5
Operating pressure, MPa	0.1-0.2	10–21
Temperature, °C	480-540	260–430
Conversion to gasoline, wt.%	50-80	30–100
Major products	gasoline, fuel oils	LPG, naphtha, jet fuel, lubricating oils

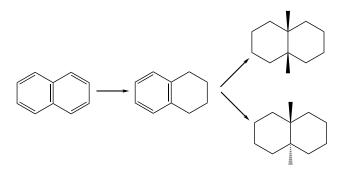
**Table 15.5** A comparison of characteristics of catalytic cracking and hydrocracking operations.



**Figure 15.11** Hydrogen atoms formed by dissociative chemisorption of  $H_2$  on the catalyst, "cap" the methylene groups formed by C–C bond cleavage to form the stable hydrocracking products.

## 15.2.6 Hydrogenation

Hydrogenation converts aromatic compounds to hydroaromatics or cycloalkanes, and alkenes to alkanes. For example, it can be used to improve the smoke point of jet fuels, by reducing the concentration of aromatic compounds, and to improve the cetane number of diesel fuels, by eliminating low-cetane aromatics. Typical catalysts are platinum or palladium, or their alloys, on silica or alumina supports. Taking naphthalene as an example, the initial product of hydrogenation is tetralin; with further hydrogenation, *cis*- and *trans*-decalin are produced.



#### 15.2.7 Sources of hydrogen

Any consideration of use of external sources of hydrogen in refining operations must eventually address the question of where the hydrogen will come from. In the past, when aromatics were acceptable components of gasolines – indeed, welcomed for their high octane ratings – catalytic reforming units could be run to achieve high yields of aromatics in the gasoline, and hence also be a net producer of hydrogen. Hydrogen from the catalytic reformer could then be used in other sections of the refinery. Today this is not the case, because it is intended to minimize aromatics formation in catalytic reforming. The reformer no longer does double duty as a source of high-octane gasoline *and* hydrogen. Fortunately, several other routes to hydrogen are available.

If natural gas is available, the best route is steam reforming of methane, e.g.

$$CH_4 + H_2O \rightarrow CO + 3H_2.$$

This reaction runs in the presence of a nickel catalyst at 750–850 °C and 3 MPa. In a subsequent step, the water gas shift reaction (Chapter 20), carbon monoxide reacts with steam to produce hydrogen and carbon dioxide.  $CO_2$  can be absorbed easily in amines (Chapter 10), leaving pure hydrogen. The advantages of this process derive from its being already used worldwide as the major source of hydrogen, so that the technology is readily available, and so that if a sweetened gas is used as feed, no treatment of the product is needed other than the shift reaction and  $CO_2$  absorption.

The reaction illustrated for methane applies to all hydrocarbons. For a generic hydrocarbon of composition  $C_x H_v$ , the equation

$$C_xH_y + xH_2O \rightarrow xCO + (x+y/2)H_2$$

applies. Materials such as propane, butane, or naphthas can be steam-reformed and serve as sources of hydrogen.

Reaction of steam with hydrocarbons is endothermic, so requires a continuous heat source for operation. With natural gas, LPG, or naphthas as feeds, the steam reforming reactor is heated externally. With heavier hydrocarbon feeds, such as fuel oils, the same chemistry applies, but the strategy for conducting the reaction changes. In this case, the process heat is obtained by a burning a portion of the feed inside the reactor, simultaneously with the reaction of the remainder of the feed with steam. That is, the hydrocarbon feed, steam, and air or oxygen are all fed to the reactor. Such an approach is called a partial oxidation process.

In petroleum refining, it makes sense for hydrogen generation to use as the feed some material readily available in the refinery, such as LPG, naphtha, or a low-value fuel oil. But, almost any carbon-containing feed will react with steam and air or oxygen to produce a mixture of carbon monoxide and hydrogen that can be shifted and purified to yield pure hydrogen. These feeds include coal, biomass, and various kinds of waste. When the feed is a solid, or a very heavy liquid, the partial oxidation process is usually referred to as gasification. Coal and biomass gasification are treated in Chapter 19.

Electrolysis of water provides another prospective route to hydrogen production:

$$2 \operatorname{H}_2 \operatorname{O} \rightarrow 2 \operatorname{H}_2 + \operatorname{O}_2.$$

At first, there might seem to be little reason to consider this option, especially when steam reforming, partial oxidation, or gasification can surely be applied to some low-value feed available in a refinery. But, electrolysis offers the potential of reducing the carbon dioxide emissions from a facility (i.e. reducing its carbon footprint), if the electricity used in this step comes from generating plants that do not themselves produce  $CO_2$ , i.e. nuclear, hydroelectric, solar, or wind. Co-locating a refinery and a nuclear power plant offers the double advantage of taking "zero-carbon" electricity for electrolytic production of hydrogen, and using some of the waste heat from the nuclear side to supply process heat for some of the refining operations, thereby eliminating  $CO_2$  production from fired heaters.

## Notes

- [A] Sir Frank Whittle (1907–1996) is generally considered to be the inventor of the jet engine. The German engineer Hans von Ohain is also credited with the invention, or as a co-inventor, though it seems that Whittle's work deserves priority. Frank Whittle worked out most of the principles of jet propulsion of aircraft in a thesis – some sources refer to it as a term paper – written while he was a student at the Royal Air Force's training school. Whittle's design for a jet engine was patented in 1930. Whittle was co-founder of a company to manufacture jet engines; their first order was for *one* engine. When the first experimental jet plane flew for the first time, an onlooker exclaimed, "Frank, it flies!" Whittle's response was, "That was what it was bloody well designed to do, wasn't it?"
- [B] This is not to imply that the same engine can operate on all these different fuels. As is true of other combustion devices, possibly even more important, the engine design must be carefully mated to the fuel that is going to be used in it, and vice versa.
- [C] An entirely different smoke point is used in the chemistry of fats and oils. There, the term refers to the temperature to which the oil or melted fat can be heated without starting to smoke. The smoke point used in this context is expressed in temperature units, and as a rough rule occurs well below the boiling point of the liquid.
- [D] One of the early fuels, JP-3, which came into use shortly after World War II, was made from the entire boiling range of gasoline and kerosene. The rapid vaporization of this fuel as the pressure was reduced when the aircraft was climbing to altitude resulted in considerable foaming. Much of the liquid fuel was lost, as was all of the fuel that had vaporized. The pilot could reach operational altitude to find that a third to half of the fuel was already gone. This problem rather significantly reduced the operational range and duration of the flight.
- [E] Rudolf Diesel (1858–1913), a German engineer born in Paris, decided on a career in engineering in his early teens. His first engineering work was in refrigeration, with his professor and mentor Carl von Linde, who himself gained fame for gas separation and refrigeration technologies. Diesel then developed a "steam" engine that operated on ammonia vapor rather than actual steam; this engine exploded. His first publication relating to the engine that now bears his name was in 1893. Demonstrating his engine running on peanut oil at the Paris Exposition in 1900, Diesel predicted that plant oils would become an important source of liquid fuels; a century later we are witnessing the steady expansion of biodiesel fuels. Diesel also predicted that his engine would become the most important one for transportation,

a claim thought to be ludicrous in the age of steam, sail, and horses. Except for a few applications, such as aircraft, the world now is "dieselizing," with diesel engine applications in virtually every segment of transportation.

- [F] Actually, the small engines used in model airplanes operate in exactly this way, because they have an almost constant load and run at the same speed all the time.
- [G] In the past decade, several interesting approaches have been developed for using absorption to achieve deep desulfurization of fuels, by removing such refractory sulfur compounds as 4,6-dimethyldibenzothiophene. One approach uses transition-metal based materials as the absorbents, including palladium compounds on silica gel, and nickel compounds on alumina. A different approach relies on ionic liquids, such as a mixture of 1-n-butyl-3-methylimidazolium chloride and 1-ethyl-3methylimidazolium chloride.
- [H] The law of diminishing returns originated in economics, often related to manufacturing or production. There, it was considered that if all but one of the factors affecting, say, manufacturing a particular item were to be held constant, and one was varied, each additional unit of the variable input (which could be labor hours, as an example) yields smaller and smaller gains in productivity. In physical fitness training or exercise, the expression, "No pain, no gain," is sometimes used. The law of diminishing returns is sometimes expressed in these terms as "The gain isn't worth the pain."
- [I] Thiophene, along with the related compounds furan and pyrrole, is an aromatic compound, sometimes referred to as a heterocyclic aromatic or heteroaromatic compound. In these compounds, the carbon atoms are  $sp^2$  hybridized as in the more familiar benzene. Each of the carbon atoms contributes a single electron to a system of  $\pi$  orbitals formed from the unhybridized *p* orbital perpendicular to the plane of the ring. In addition, the heteroatom, e.g. sulfur, contributes a lone pair of electrons to a *p* orbital perpendicular to the ring. Thus there are six total electrons in the delocalized  $\pi$  system, fulfilling the Hückel criterion for aromaticity.

#### **Recommended reading**

- Ancheyta, Jorge and Speight, James G. Hydroprocessing of Heavy Oils and Residua. CRC Press: Boca Raton, FL, 2007. A useful monograph on hydroprocessing of the heavy and hard-tohandle materials.
- ExxonMobil Aviation. *World Jet Fuel Specifications*. 2005. A very useful compilation of these specifications, available on the web at www.exxonmobil.com/AviationGlobal/Files/World-JetFuelSpecifications2005.pdf.
- Froment, G.F., Delmon, B., and Grange, P. *Hydrotreatment and Hydrocracking of Oil Fractions*. Elsevier: Amsterdam, 1997. An edited collection of about 60 original research papers in this field.
- Gary, J.H. and Handwerk, G.E. *Petroleum Refining*. Marcel Dekker: New York, 1984. An excellent source of information on refining processes. Chapters 8 and 9 apply to the present chapter.
- Guibet, Jean Claude. *Fuels and Engines*. Éditions Technip: Paris, 1999. This excellent book, though of course not covering the most recent advances, provides a comprehensive look at hydrocarbon and biofuels, and the interdependence of fuel properties with engine design and operation. Chapters 4 and 7 relate to the present chapter.

- Meyers, Robert A. *Handbook of Petroleum Refining Processes*. McGraw-Hill: New York, 1997. A useful trove of details on specific refinery processes. Parts 6, 7, and 8 relate to the present chapter.
- Speight, James G. *The Chemistry and Technology of Petroleum*. Marcel Dekker: New York, 1991. Chapter 16 of this very useful book provides a thorough overview of hydroprocessing.

# 16.1 Thermal cracking

In the progression through the oil window, thermally driven reactions break kerogen and larger hydrocarbon molecules into smaller ones. In a refinery, analogous processes take some of the heavier products and break them into smaller molecules. This shifts the molecular weight downward, increasing the amounts of relatively small molecules boiling in the gasoline range. To operate on a human rather than a geologic time scale requires running at much higher temperatures than are encountered in the oil window. Processes that rely entirely on heat for breaking down large petroleum molecules into smaller ones are called thermal cracking.

With the steady increase in use of automobiles and trucks in the early decades of the past century, market demand for gasoline exceeded what could be supplied by straightrun gasoline, even augmented with natural gasoline. Cracking processes can increase the relative proportion of molecules in the  $C_5$ - $C_{10}$  range, at the expense of larger molecules in products having a lower value than gasoline.

Refinery cracking processes are of two types, thermal (that rely entirely on temperature to drive the cracking reactions) or catalytic. Chapter 14 included a discussion of catalytic cracking reactions and processes. Thermal processes were developed starting around 1913. Numerous thermal cracking processes were developed in the early decades of the twentieth century. They helped meet the increasing demand for gasoline in the 1920s and 30s. The process developed by C.P. Dubbs [A] provides an example (see Figure 16.1).

The basic purpose of thermal cracking, before about 1950, was to enhance the yield of light and middle distillates from the heavier components. Depending on feedstock and cracking conditions, thermal cracking could roughly double the output of gasoline relative to straight-run gasoline. Blending straight-run gasoline with thermally cracked product can raise the yield of gasoline to about 40% and its octane rating to  $\approx$ 75. Thermal cracking is inevitably accompanied by formation of aromatics, which contribute to enhancing the octane number. Most thermal cracking processes for producing light distillates were replaced by catalytic cracking beginning in the 1940s. Today, thermal cracking remains a useful process for viscosity reduction, described below, and has enormous importance for manufacturing ethylene for the petrochemical industry.

The chemistry of thermal cracking is not much different from the radical reactions of kerogen catagenesis (Chapter 8). The tendency for compounds to crack follows the order alkanes > alkenes > alkadienes > cycloalkanes > aromatics. The tendency of an oil to undergo cracking, and how it depends on composition, can be illustrated using the ternary composition diagram introduced in Chapter 11 (Figure 16.2).

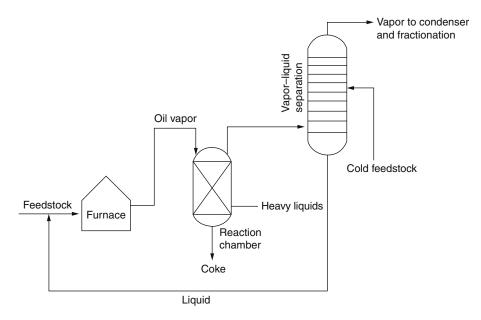


Figure 16.1 Process flow for the Dubbs thermal cracking process.

As a rule, paraffinic crudes are preferred feedstocks for cracking.

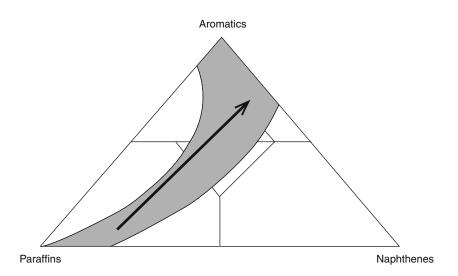
Initiation comes from homolytic scission of a C–C bond. A radical produced during initiation abstracts hydrogen from a second molecule, e.g.

The newly produced  $2^{\circ}$  radical can undergo  $\beta$ -bond scission to a 1-alkene and a  $1^{\circ}$  radical:

 $CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$  $\rightarrow CH_{3}CH_{2}CH_{2}CH_{2}\bullet + CH_{2}= CHCH_{2}CH_{3}.$ 

The new 1° radical then participates in further propagation reactions. Termination by radical combination could, in principle, bring cracking to a halt fairly quickly, because recombination reactions are very rapid. However, in industrial cracking processes the concentration of non-radical hydrocarbons is much greater than the concentration of radicals. Collision of a radical with a hydrocarbon, for propagation, is more likely than termination via collision of a radical with another radical.

The severity of the process – time, temperature, and pressure – fixes the conversion to products, and the composition, structures, and properties of the products. Running a cracking process at higher temperature reduces the residence time needed to achieve a desired level of conversion. Time and temperature are not fully interchangeable; that is, a short time at high temperature does not necessarily get to the same point as a long residence time at low temperature. One might achieve the same conversion, but not necessarily the same product slate. This is because different reactions for initiation and propagation can be favored at different temperatures. As a result, the contribution of a given product to the overall product slate can change as reaction temperature changes.



**Figure 16.2** The tendency of oils to undergo cracking, as related to their position on the ternary composition diagram of Figure 11.2.

Generally, low pressures (< 0.7 MPa) and high temperatures (>500 °C) favor formation of low molecular weight products. Thermal energy available at such high temperatures drives endothermic bond-breaking reactions. Low pressures favor formation of gases or vapors. In contrast, running thermal cracking at, say, 3–7 MPa and <500 °C would reduce formation of light materials. The residence time necessary to achieve a given conversion depends on how labile or refractory the feedstock is with respect to cracking. If the feedstock cracks only to a limited extent, recycling the heavier, uncracked material offers the possibility of increasing overall conversion. However, this strategy works only to an extent, because with each pass through the reactor, the refractory, hard-to-crack compounds become increasingly concentrated in the heavy recycle stream. That is, the recycle stream can become more and more difficult to crack with each cycle.

Low-pressure operation enhances formation of alkenes in the light products. Alkenes are undesirable in gasoline, jet fuel, and diesel fuel because of their tendency to oligomerize to gums, especially during storage in the presence of air. However, formation of alkenes during cracking is not necessarily undesirable. Smaller alkenes, such as propylene, have many uses in the chemical industry. Among the many products that can be made from just this one starting material are polypropylene, acetone, acrylonitrile, acrylic acid, isopropanol, and propylene glycol [B]. Mild thermal cracking of  $C_{14}$ – $C_{34}$  alkanes produces  $C_6$ – $C_{20}$  alkenes. Higher alkenes have boiling points so close to the parent alkane that separation is impractical. For example, the boiling points of the  $C_7$  compounds are heptane, 98 °C; 1-heptene, 94 °C; 2-heptene, 98 °C; and 3-heptene, 96 °C. Alkenes have higher octane numbers than the corresponding alkanes. Their presence in gasoline produced by thermal cracking increases the octane number relative to straight-run gasoline, despite their tendency to gum formation.

The earliest thermal cracking process developments were batch processes, from which it can be difficult to achieve high throughputs. C.P. Dubbs developed continuous-flow thermal cracking. Mixed-phase cracking, intended to produce primarily

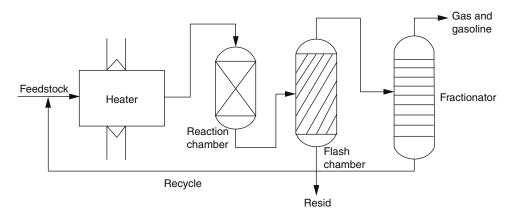


Figure 16.3 Process flow for mixed-phase cracking.

gasoline, represents continued evolution of such operations. Figure 16.3 shows a block flow diagram for mixed-phase cracking.

The feedstock can be kerosene, gas oil, resid, or sometimes even crude oil itself. After rapid pre-heating, the feed flows to the reaction chamber, maintained at 400-480 °C and 2.5 MPa. The specific temperature depends on the feedstock. The pressure is selected to maintain a virtually homogeneous phase with a high liquid-to-vapor ratio. Overhead from the flash chamber goes to a fractionating tower, to obtain gasoline. Flash chamber bottoms are used as heavy fuel oil; fractionating tower bottoms are recycled.

Figure 16.4 shows a process for continuous thermal cracking of resids. Resid is heated by mixing with the already cracked products in the distillation tower. The principal products are gasoline and middle distillates. Heavy fuel oil can also be recovered.

# 16.2 Visbreaking

Within a given family of compounds, reducing molecular size also reduces viscosity. In dealing with highly viscous process streams or crude oils, it is helpful to "break" the viscosity by reducing the size of the molecules in the liquid. This viscosity breaking, or visbreaking, reduces the viscosity, boiling range, and pour point of materials such as resids. That all of these changes can be achieved in one process results from the relationships between these physical properties and molecular size or structure introduced in Chapter 9. Visbreaking aims at reducing the viscosity of a fluid so that less energy is needed for it to be pumped, or to make the fluid more amenable to transportation by pipeline. Candidates for visbreaking include resids, crude oils, or oil from oil sands. Visbreaking is also used for production of gas oils as feedstocks to catalytic cracking.

High viscosity in hydrocarbon liquids results from intermolecular interactions and from entanglement of long molecular chains, present either as alkanes or as alkyl side chains on cycloalkane or aromatic molecules. Thermal cracking cleaves a portion of the large molecules, or reduces length of side chains. In very large molecules that have

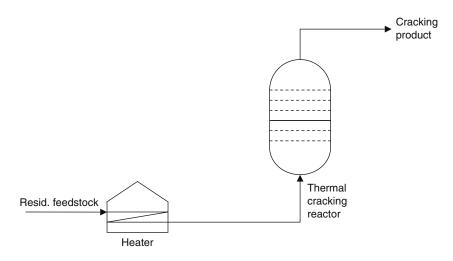


Figure 16.4 Process flow for simple thermal cracking of resids.

aromatic structures held together by crosslinks of polymethylene chains, heteroatoms, or both, mild thermal cracking can break some of these linkages, achieving significant reduction in molecular size. As a result, even seemingly small conversions to low-boiling gasoline or naphtha can still effect substantial reductions in viscosity. Reduction in viscosity by visbreaking is accompanied by a reduction in the measured pour point, and a general improvement in the low-temperature properties of the material.

Unlike the thermal cracking processes discussed previously, visbreaking aims at improving the viscosity behavior of the feedstock. Converting the feedstock into lowboiling fuels is not a primary consideration. Figure 16.5 shows a block flow diagram of a visbreaking process.

Visbreaking occurs as the feedstock flows through the reaction furnace. Temperature depends on the feedstock to be cracked. For example, an atmospheric distillation resid might be heated to 500-525 °C; the temperature at the exit will be about 440-445 °C. Reaction severity is controlled by flow rate or residence time in the furnace, typical values being about 1–3 min. Operating pressure is selected to help control residence time, but also to help control extent of vaporization. With resid, operating pressure could be in the range 0.35–0.70 MPa, the highest pressures used being  $\approx$ 5 MPa. Since there is no external hydrogen source, formation of some light distillate products must inevitably be accompanied by concurrent formation of carbon-rich products, i.e. coke. Running at short residence time helps reduce coking in the furnace. Nevertheless, about once every three to six months the furnace must be "de-coked." Cracked products from the reaction chamber go to the flash chamber. The overhead is separated into gasoline (sometimes known as visbreaker gasoline) and light gas oil; the bottoms go to a vacuum fractionator to produce heavy gas oil and vacuum tar. Visbreaker gasoline is blended with other sources of gasoline within the refinery to make the gasoline products eventually sold to consumers.

More severe thermal cracking of straight-run heavy gas oil affords a range of products, including ethylene, LPG, naphtha, kerosene, and light gas oil as middle distillates, and a material called thermal tar. Thermal tar is commonly highly aromatic,

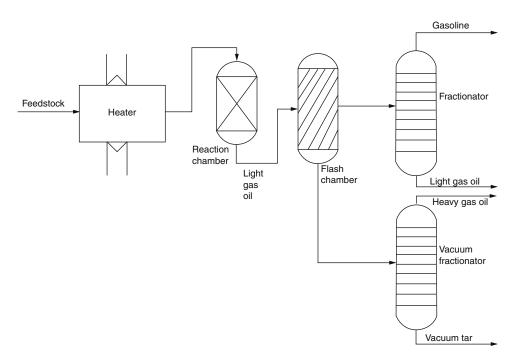


Figure 16.5 Process flow for a visbreaking operation.

highly viscous, and high-boiling. Thermal tar represents the carbon-rich or low H/C products from the inevitable internal hydrogen redistribution processes accompanying the radical reactions involved in thermal cracking, which accompany the formation of the more desirable light products of high H/C ratio.

Visbreaking of vacuum resid produces  $C_3$  and  $C_4$  gases, naphtha, middle distillates, and fuel oil. Internal hydrogen redistribution leads to formation of coke. This coke has little, if any, value as a carbon material, but can be a useful solid fuel. Coil visbreaking passes vacuum resid through a coil of piping at 475–500 °C with a residence time of 1–3 min. Fractionation of the output yields some gas, gasoline, light gas oil, heavy gas oil, and No. 6 fuel oil. An alternative process, soaker visbreaking, heats the resid to lower temperatures and longer reaction times to achieve essentially the same end. Milder visbreaking produces No. 6 fuel oil, along with a small amount of coke.

## 16.3 Coking processes

Severe thermal cracking is accompanied by production of significant amounts, often >25%, of coke. Coking processes can be run with two different aims in mind. First, it might be the intent to subject heavy feedstocks to extensive thermal cracking to increase the yield of liquids. In that case, the coke is the inevitable by-product. If no other applications can be found, the coke can be burned as a fuel for generating process heat or raising steam. The second aim would be to run a coking process to make a marketable coke product, with liquids as the by-product.

Throughout fuel chemistry and technology, the word coke occurs in many contexts, not always used correctly. Coke is a solid carbonaceous material that formed from a fluid phase, or that passed through a fluid phase during its production. The term petroleum coke is used to describe those carbonaceous solids made by severe thermal processing of various fractions of petroleum. Besides reminding us of the source of the feedstocks used to make these cokes, the adjective petroleum also helps distinguish them from metallurgical coke that is manufactured from coal [C]. (Metallurgical coke is discussed in Chapter 23.) In the past, coking was sometimes referred to as the "refiner's garbage can," in the sense that any products of low value, or that have no market at all, could be converted into coke while eking out a little more liquid for the refinery. However, for production of high-value petroleum cokes, monitoring and controlling the quality of the feedstock used to make the coke become very important.

The yield of coke is usually proportional to the carbon residue produced when the feedstock is evaluated in various standardized laboratory tests, such as the Conradson carbon residue test. In this test, a weighed amount of filtered sample is placed in a porcelain crucible that is then put inside an iron crucible. This dual-crucible assembly is put inside a third iron crucible, packed with sand. The apparatus is heated with a gas-fired burner until the sample begins to smoke, then the vapors driven off by cracking are burned, and finally the outermost crucible is heated red hot for a specified time. The amount of carbon recovered at the end of this test is the Conradson carbon residue. Alternative tests have been, and are, in use. The so-called micro carbon residue is increasing in popularity because it can be run in a thermogravimetric analysis instrument, with a smaller sample size, less labor, and in less time.

#### 16.3.1 Delayed coking

The "delay" in the term delayed coking comes from the way in which the process is run. The feedstock is heated in a furnace at short residence times, about 3 min, but the coking does not take place until the hot feedstock is passed into a coke drum downstream of the furnace, giving a delay between heating the feed and the actual formation of the coke itself.

Delayed coking, a severe thermal cracking process, upgrades and converts resids or other heavy fractions into liquid and gaseous products, along with producing petroleum coke. Delayed coking provides the refinery with additional distillate products. Internal hydrogen redistribution forms the carbon-rich coke and relatively hydrogenrich liquids and gases. Delayed coking operations have very long residence times ( $\approx$ 18–24 hr) to insure completion of the cracking and hydrogen redistribution processes. About 75% of the feed is converted to lighter products, and the remaining 25% forms coke. Three kinds of coke can be produced, depending on the feedstock and coking conditions. They have various names, often being called shot coke, sponge coke, and needle coke. Shot coke has the lowest value and is used only as a cheap solid fuel. Sponge coke, the intermediate grade, is primarily used as the raw material for making carbon anodes used in electrolytic smelting of aluminum. The premium grade is needle coke, used to make synthetic graphite for various applications, including arc-furnace electrodes.

Delayed coking (Figure 16.6) is a semi-continuous (or semi-batch) operation, in that the feedstock is introduced continuously, but the coke is allowed to accumulate in

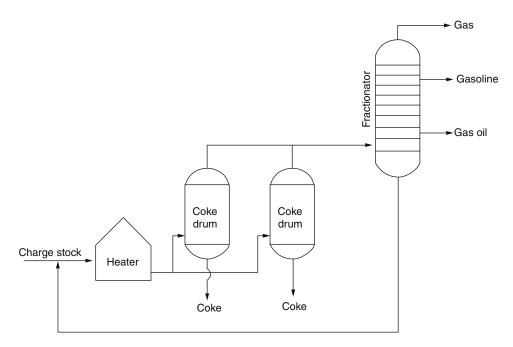


Figure 16.6 Process flow for delayed coking.

batches that are removed at intervals of 18–24 hours. Because of the semi-continuous process, there are at least two coke drums, so that one can be filling with coke while coke is being removed from the other. The temperature in the coke drums is  $\approx$ 450 °C, and pressure is 0.1–0.6 MPa.

The charge is heated rapidly to >475 °C at 70–200 kPa. The preheated feed passes into the bottom of a large, cylindrical coke drum, which might be 4-10 m diameter and 18–35 m tall. Though the charge reaches cracking temperatures in the preheater furnace, coke formation begins in the coke drum. The light, cracked products normally leave the reactor quickly. Coke builds up in the coke drum until it is filled. A delayed coking unit has two, or possibly four, coke drums. When one drum has filled, the preheated feed is switched to the other, empty drum. The very long reaction times in the coke drum convert the liquid feed to gases, distillates, and coke. Steam is passed through the filled drum to vaporize any feedstock that has not converted, and to drive out light products that have not escaped. Coke is removed using water or steam lances at high pressure (>20 MPa) to cut the coke mass apart and away from the wall of the drum. Vapor products come off the top of the coke drum at  $\approx$ 435 °C and are quenched by contact with colder oil. Unfortunately, the hydrogen redistribution and radical termination reactions that produce the coke also tend to retain any sulfur, nitrogen, or metals in the feed, so the coke is enriched in these elements, relative to their concentrations in the feedstock.

Much of the chemistry of delayed coking involves the same sorts of radical reaction and hydrogen redistribution that have been discussed several times. The reactivity of feedstocks is closely related to the ease of radical initiation, which derives from the composition and molecular structures of the feeds. Several kinds of thermally driven radical propagation reaction then occur. These include: cracking of alkyl side chains on alkylaromatic molecules; aromatization of cycloalkanes; loss of hydrogen from alkanes to form alkenes, dienes, trienes... and their cyclization to aromatics; oligomerization of alkenes or dienes; and condensation of small aromatic structures, via dehydrogenative polymerization, into bigger, higher molecular weight aromatics. Termination reactions involve hydrogen transfer within the reacting medium and radical combination reactions. As long as it is possible to sustain hydrogen-transfer, the viscosity of the liquid phase remains relatively low. Keeping viscosity low for a prolonged period of time is important for the processes about to be described.

A consequence of hydrogen transfer is a steady accumulation of compounds of low H/C, mainly aromatics, in the liquid phase. While the lighter products, with H/C higher than the feedstock, escape from the coker, these remaining heavier molecules continue to condense to form structures of increasing molecular weight. Eventually the concentration of heavy material reaches a point at which phase separation occurs, giving a second liquid phase denser and more aromatic than the original liquid. The separation of the phases depends on the solvent characteristics of the parent liquid. On the basis of the useful rule that like dissolves like, if the original liquid is itself highly aromatic, it is more likely to retain these bigger, high molecular weight aromatics in solution. A heavy aromatic material separates more easily from an original liquid phase that was highly paraffinic.

The new second, separate liquid phase is called mesophase. The name implies that mesophase is an intermediate phase between the comparatively small molecules in the feedstock and the fully solidified coke. The large polycyclic aromatic molecules that formed as a result of the various radical reactions are called mesogens. Mesophase represents regions of molecular alignment in the liquid. Mesophase growth by coalescence can form, ultimately, very extensive regions. Solidification then results in an anisotropic solid coke. Since extent of mesophase development is a function of the molecular structures originally in the feedstock, their reactivities, and the viscosity of the liquid, all of which can vary, cokes of different degrees of molecular alignment can be produced.

This new phase is a liquid crystal; i.e. it has fluid properties of a liquid but optical anisotropy and structural order of a solid. Mesogens are lamellar, nearly flat polycyclic aromatic hydrocarbons, which tend to stack in parallel alignment and eventually precipitate as spherules. The emergence of mesophase spherules as a separate phase results from homogeneous nucleation within the parent liquid.

Forming an ordered mesophase is not always possible. First, not all of the molecular configurations that develop are necessarily flat. Some may show pronounced curvature, due to the incorporation of heteroatoms, five-membered rather than six-membered rings, or some residual tetrahedral  $sp^3$  carbon. Such structures have two limitations: either they cannot condense into larger, planar structures, or if they do condense, the large high molecular weight condensation products themselves are unable to align. The ability to achieve the necessary parallel alignment of near-planar polycyclic aromatic hydrocarbon sheet structures in the liquid depends on the reactivities of the components of the liquid and the viscosity of the liquid phase. Viscosity and chemical reactivity are not necessarily related or interdependent, even though both affect the eventual outcome of coking.

As coking proceeds, the mesophase spherules gradually coalesce into larger structures. The size of these structures again depends on reactivity, viscosity of the fluid

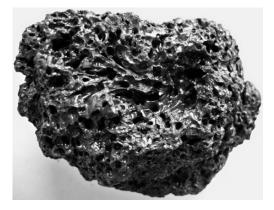


Figure 16.7 Sponge coke produced in delayed coking.

medium, and whether enough time is available for growth. The evolution of gases and vapors through the mass of material undergoing coking may also help achieve alignment of the growing structures. Eventually these molecules become so large that a carbonaceous solid, the coke, is formed as the product.

Coking at high temperatures, e.g. about 500 °C, enhances the rate of mesophase formation. However, the rate of initiation can outpace the ability of hydrogen transfer to stabilize radicals. As a result, radical combination reactions become the dominant termination process, leading to a rapid increase in viscosity. The viscosity increase has two consequences: there is not sufficient time for stacking of large aromatic molecules into ordered lamellae nor for coalescence of mesogen molecules; and, rapid increase in viscosity leads to a solidification of the system, possibly earlier (in terms of the chemical processes) than would have been wanted. Coking at high pressure delays solidification. High pressure retards gas and vapor evolution. Because more of the light fractions are retained in the system, low viscosity can be maintained for a relatively long time. This situation provides time for the formation of mesogens, and growth and coalescence of mesophase. However, because gas evolution is diminished, structural rearrangements thought to be effected by passage of gas through the coking system may not take place. A less-ordered structure forms.

Coking of vacuum resid with high heteroatom, metal and asphaltene contents produces coke that is suitable only for fuel use. This material, often called shot coke, forms as agglomerates of spheres 1–2 mm in diameter, somewhat resembling the pieces of shot in shotgun shells. Shot coke has low value, being marketed only as a fuel. For that reason, this product is sometimes also known as fuel coke.

Sponge coke, sometimes called anode coke or regular coke, comes from delayed coking of vacuum resids. It is porous and produced in irregularly shaped lumps (Figure 16.7). Cokes from feedstocks with relatively low heteroatom and asphaltene contents, and high aromatic contents, can be suitable as a raw material for production of aluminum-smelting anodes [D].

Needle coke is a premium coke from delayed coking of highly aromatic feedstocks. Needle coke is used to make synthetic graphite. The largest single market is in production of electrodes for electric arc furnaces, as would be used, e.g. in melting of steel scrap for re-use in steel production. Coke taken directly from the delayed coker, called



Figure 16.8 Macroscopic view of a piece of needle coke from delayed coking.



**Figure 16.9** A photomicrograph of the structure of needle coke, showing elongated "needle-like" regions.

green coke, must be calcined at 1000–1400 °C to expel any remaining volatile components and to increase its density before it can be used in production of synthetic graphite. Figure 16.8 provides a macroscopic image of needle coke.

Unlike sponge coke, which does reasonably resemble a natural sponge organism, there is nothing needle-like about a piece of needle coke. The name derives from the textures in the coke that are evident on optical microscopy (Figure 16.9) which, with a bit of imagination, resemble needles. The good graphitizability of needle coke derives from the preferred orientation of its microcrystalline structure shown in Figure 16.9.

Feedstocks for needle coke production include: decant oil from catalytic cracking; thermal tar from thermal cracking; and ethylene tar, the highly aromatic residue thermal cracking units use to produce ethylene. It is essential that the feedstock have high aromatic content, low content of heteroatoms, and low asphaltene content. FCC decant oil is preferred for needle coke production. Sulfur in the coke is especially undesirable. Normally needle coke is ground and mixed with a pitch to bind the particles together. This coke-pitch mixture is then shaped into the desired graphite product (e.g. an electrode). The shaped artifact is baked at  $\approx 1500$  °C before final

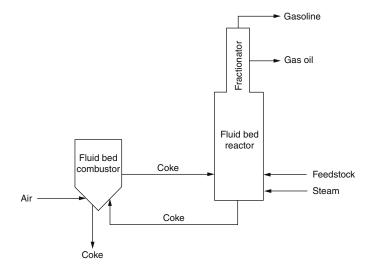


Figure 16.10 Process flow for fluid coking.

graphitization at  $\approx 3000$  °C. When cokes containing sulfur are heated to the baking temperature, the remaining sulfur-containing compounds decompose. Their evolution as vapors causes a rapid and irreversible expansion of the shaped carbon artifact, ruining it for any further production. This phenomenon is known in the graphite industry as puffing.

#### 16.3.2 Fluid coking and Flexicoking

Fluid coking involves spraying the feedstock into a fluidized bed of already existing coke particles. The coke particles in the bed have diameters of about 100–600  $\mu$ m. Reaction temperatures are in the range 510–535 °C. Coking of the feedstock occurs on the surface of the coke particles in the bed. Vapors of light products are quenched by bringing them into contact either with the feedstock or with previously condensed liquid products. Figure 16.10 provides a process diagram for a fluid coking operation.

Fluidized beds offer very good heat transfer properties. Higher temperatures can be attained than are normal in delayed coking. In turn, these higher temperatures drive cracking to a greater extent. Using a fluidized bed reactor also reduces residence time of the light products, relative to delayed coking. The shorter residence time results in less coking. Overall, fluid coking gives a lower coke yield, but higher yields of liquids. Process heat is obtained by burning some of the coke. Fluid coking is useful for converting high-sulfur feedstocks into fuel coke.

Flexicoking is a variation of fluid coking. A process diagram is given in Figure 16.11. Flexicoking combines the fluidized-bed coking process with a gasifier. This produces a clean fuel gas, albeit usually of low calorific value, for use in the refinery. The gasifier would also be a fluidized-bed reactor, in which the coke reacts with steam and air at temperatures up to 1000 °C. When air is used in the gasifier, the product gas is diluted heavily with nitrogen, which might be  $\approx 50\%$  of the total gas. The combustible components are carbon monoxide and hydrogen, at 15–20% each, and small amounts of methane. The gas might also contain  $\approx 10\%$  carbon dioxide, another inert diluent. Any

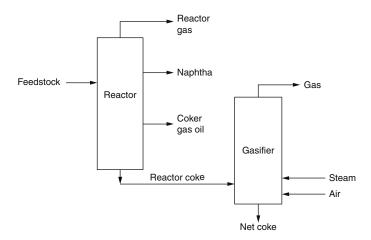


Figure 16.11 Process flow for flexicoking.

hydrogen sulfide in the gas stream, resulting from sulfur in the coke, can be removed by scrubbing before the gas is used.

## Notes

- [A] The father-and-son team of Dubbses developed thermal cracking processes around 1914. The father, Jesse, was a native of the Pennsylvania oil-producing region. He named his son Carbon Petroleum Dubbs, who, not unreasonably, seemed to prefer to be known as "C.P." Father and son were involved in the formation of a company called Universal Oil Products; rather than producing and marketing petroleum products, this company was (and is) mainly in the business of developing refining processes and licensing them to other companies. Today, Universal Oil Products is known as UOP, a large, multi-national company still active in refining and allied process technologies, such as gas processing. C.P.'s unusual name proved to be no handicap in his profession; he is reputed to be one of the rare individuals who became a millionaire during the Great Depression. Remarkable stories about the family abound; it's claimed that C.P.'s son and grandson were also named Carbon; another version indicates that C.P. had two daughters, whom he named Methyl and Ethyl.
- [B] This array of products, all of which come from propylene that in turn comes from petroleum, supplies us with: plastics, from polypropylene, acrylic acid, and methyl methacrylate (made from acetone); acrylic fibers, carbon fibers, and synthetic rubber, from acrylonitrile; solvents and cleaning fluids, in the form of acetone and isopropanol; and antifreeze and aircraft de-icing fluid, from propylene glycol. This is not a complete list of the commercially valuable products that can be made from propylene, nor is it close to a complete list of the uses of just the six compounds mentioned here as examples. When supplies of petroleum inevitably decline in the future, we are going to run out of a lot more than just liquid fuels.

- [C] The irony in this terminology is that the dominant uses of petroleum coke are actually metallurgical; in a broad sense, petroleum coke *is* metallurgical coke. By far the dominant markets for petroleum coke are the aluminum and steel industries.
- [D] Some form of carbon can often be an effective, and cheap, reducing agent for obtaining metals from their oxide ores. The utility of carbon in this application is limited because many metals, aluminum among them, form stable carbides. Direct reduction of the oxide with carbon would not be a useful route to metal. Virtually all the world's aluminum is produced from the Hall-Héroult process. Aluminum oxide, purified from its naturally occurring ores, such as bauxite, is dissolved in molten cryolite, Na<sub>3</sub>AlF<sub>6</sub>. An electric current is passed through this solution between electrodes made of carbon. Metallic aluminum deposits at the cathode. Several materials, including anthracite, can be used as the cathode. Anodes are made from sponge coke, formed into shape with pitch as a binder, and then carefully shaped and baked. At the anode, oxygen reacts to produce carbon dioxide. The products of reaction are aluminum and CO<sub>2</sub>, and the net process can be represented as  $2Al_2O_3 + 3 C \rightarrow 4 Al + 3 CO_2$ . Carbon is consumed in the process, so anodes must be replaced periodically. Because impurities, such as iron or silicon, in the anode could contaminate the aluminum, the quality of the sponge coke must meet stringent standards to be acceptable as anode-grade coke.

#### **Recommended reading**

- Adams, Harry. Delayed coking: practice and theory. In: *Introduction to Carbon Technologies*. (Marsh, Harry, Heintz, Edward A., and Rodríguez-Reinoso, Francisco; Eds.) University of Alicante: Alicante, 1997; Chapter 10.
- Freeman, C. and Soete, L. *The Economics of Industrial Innovation*. Routledge: London, 1997. Chapter 4 of this book has interesting background information on the early days of thermal cracking, the coming of the Dubbses, and the eventual rise of catalytic cracking to supplant thermal processes.
- Gray, Murry R. *Upgrading Petroleum Residues and Heavy Oils*. Marcel Dekker: New York, 1994. Chapter 6 provides a useful discussion of coking and thermal cracking processes.
- Nelson, Wilbur L. *Petroleum Refinery Engineering*. McGraw-Hill: New York, 1958. Though now rather old, this book was the classic in its field, and Chapter 19, on thermal cracking processes, contains a wealth of information on this topic.
- Speight, James G. *The Chemistry and Technology of Petroleum*. Marcel Dekker: New York, 1991. Chapter 14, on thermal cracking, is relevant to the present chapter. Coke products are discussed in Chapter 20.
- Wiehe, Irwin A. *Process Chemistry of Petroleum Macromolecules*. CRC Press: Boca Raton, 2008. Gives extensive information on various aspects of processing heavy oils or heavy fractions. Chapters 8 and 9 are particularly relevant to the present chapter.

# **17** Composition, properties, and classification of coals

Among the fossil fuels, the progression from natural gas to petroleum to coal is one of increasing complexity. Even a wet, sour gas has only a small number of possible components. Once the gas has been treated and purified for distribution to consumers, it typically contains >90% of a single compound, methane. Gas contains no inorganic impurities that might leave an ash residue on combustion. Petroleum usually is a homogeneous liquid with a narrow range of elemental composition – about 82–87% carbon, 12-15% hydrogen and the balance nitrogen, sulfur, and oxygen - with atomic H/C ratio of  $\approx 1.5-1.8$ . On a molecular level, petroleum contains thousands of individual compounds, every one of which could be separated, at least in principle, using common techniques of the organic chemistry laboratory, and identified [A]. Inorganic ash-forming constituents are commonly less than 0.1%. In contrast, coals have an extremely wide range of composition, some 65–95% carbon, 2–6% hydrogen, up to about 30% oxygen, and possibly several percent each of sulfur and nitrogen. The H/C ratio is less than 1. Coals are opaque, heterogeneous solids. Coals cannot be distilled reversibly. Coals are not completely soluble in any solvent, and even the partial solubility in various solvents is an extraction of components rather than a true, reversible dissolution process. Coals have a macromolecular structure that varies from one coal to another and that has never been completely elucidated for any coal. Coals contain a variable, but appreciable, amount of inorganic material, so that burning a particular coal leaves an ash residue that represents anywhere from a few percent to over 25% of the original weight of the coal. Coals also contain some variable amount of water as they are mined from the Earth, from several percent to about 70%.

Despite the complexity of coals and the difficulties encountered in studying them, systems for classifying and describing coals are nevertheless needed. Such systems can provide a conceptual framework for organizing knowledge of coal composition and properties. In a very practical sense such systems provide the descriptions needed for legally binding buying and selling of coals.

# 17.1 Classification of coal by rank

Chapter 8 introduced the names of various kinds of coal that form during the sequence of processes associated with coalification. These coals can be identified by their position on the van Krevelen diagram (e.g. Figure 8.7). Each of the kinds of coal differs from the others in terms of carbon content; for example, a bituminous coal has a higher amount of carbon than subbituminous, but a lower amount than anthracite. Coals could then be put into these various categories on the basis of carbon content. Indeed, the carbon content of coal is a handy and useful way of classifying coals, especially for laboratory research in coal chemistry.

For practical, industrial use, coals are classified by rank based not on carbon content but rather on behavior during utilization. The considerations involve the amount of heat liberated when the coal is burned, the behavior of coal during combustion, and, for some coals, their application to making metallurgical coke. Many countries have their own sets of standards for classifying coals by rank. One widely used system is that of the American Society for Testing and Materials, almost always known by its initials, ASTM [B].

The heating value, or calorific value, is determined by bomb calorimetry. A weighed sample is burned in oxygen, and the heat liberated into the surrounding water jacket is measured. In the United States, heating value is still expressed in the old units of Btu/lb, whereas elsewhere units of MJ/kg would be used. As described later, measurements made on a sample as analyzed in the laboratory are corrected to account for the fact that the analysis sample inevitably contains some amount of moisture, and contains various inorganic components that convert to ash when the sample is burned.

All coals, as extracted from the ground, have some amount of water associated with them. Brown coals sometimes have >50% of water with the coal; i.e. the mined product is more water than coal. Heating coal in vacuum or in inert atmosphere to  $107\pm4$  °C for an hour results in a weight loss. This weight loss is said to be the moisture content of the coal, though the material that has been lost under these conditions is not routinely collected and analyzed to show that it *is* water, or that it is *only* water.

Increasing the temperature to  $950\pm20$  °C while maintaining the inert atmosphere causes a second weight loss. This treatment drives off various gaseous species, such as the oxides of carbon and a great variety of organic molecules. The compounds driven off during this test are never collected and determined individually; rather, they are lumped together under the term volatile matter. The material still remaining after the volatile matter has been driven off has the appearance of a black, carbonaceous solid. Exposure of this material to air at  $725\pm25$  °C burns off any remaining organic material, leaving behind an incombustible residue, ash. As part of this test procedure the ash is not analyzed further; usually it consists of a complex mixture of aluminosilicates, silicates, and oxides (Chapter 18). The carbonaceous, organic substances that have just been burned off were materials that resisted vaporization during the volatile matter test. In the early days of chemistry, substances that resisted phase changes were known as "fixed" [C]. This carbonaceous material is said to be *fixed carbon*. Fixed carbon is calculated easily as

$$FC = 100 - [M + VM + A],$$

where FC is fixed carbon; M, moisture; VM, volatile matter; and A, ash.

In none of these determinations are the actual chemical constituents separated and measured. For example, volatile matter often contains some carbon dioxide (among many other components), yet in the routine determination of volatile matter, carbon dioxide is never separated, collected, and reported as some percentage of CO<sub>2</sub>. In analytical chemistry, the practice of lumping a variety of components and reporting them as a single entity is known as proximate analysis [D]. The proximate analysis of coal consists of determining the moisture, volatile matter, and ash, and calculating the fixed carbon. In a sense the word *proximate* was a rather unfortunate choice, because it

sounds so much like *approximate*. A proximate analysis is not approximate analysis! The specific procedures of these determinations, as well as acceptable limits of error within or among laboratories, are rigidly controlled by the test methods established by national standards bodies such as ASTM.

Proximate analysis provides values for four parameters, but only two – volatile matter and fixed carbon – relate to the carbonaceous portion of the coal and to its combustion behavior. Coals of high volatile matter content are usually easy to ignite but burn quickly; when burned on a grate they have a large and often smoky flame. High fixed carbon content indicates coal that may be difficult to ignite but burn more slowly. A burning bed of this coal is likely to have a short, clean flame. The ratio of fixed carbon to volatile matter is called the fuel ratio of the coal. Fuel ratio gives an indication of how difficult the coal is to ignite, how rapidly it will burn out, and the quality of the flame (i.e. long and smoky or short and clean).

In contrast, not only does moisture vary from one coal to another, the moisture content of a given coal also depends on how the sample was handled and stored before being analyzed. A sample that has stood in an open container in the laboratory for several hot, dry summer days will probably have a lower moisture content than a second sample of the very same coal taken from the top of an outdoor stockpile after several days of rain. The ash value also varies from one coal to another. It too can vary within a set of samples of the same coal. For these reasons, it can be much more informative of the nature of the coal itself to compare the volatile matter and fixed carbon on a moisture-free (mf), or moisture-and-ash-free (maf) basis.

Converting some property X (i.e. volatile matter, fixed carbon, or ash) from the asreceived or as-analyzed basis to a moisture-free basis is

$$X_{mf} = 100 \bullet X_{ar} / (100 - M_{ar}).$$

Converting to moisture-and-ash-free is handled similarly:

$$X_{maf} = 100 \bullet X_{ar} / [100 - (M_{ar} + A_{ar})].$$

Ash, the residue left behind after the coal has burned, is not an inherent component of coal, though quite commonly those working with coal use the term "ash content." The ash found in the proximate analysis comes from reactions that occur to the inorganic components originally present in the coal. That is, ash is a reaction product, and, strictly speaking, there is no ash *in* coal. The reactions of some minerals during formation of ash result in changes of weight, for example the thermal decomposition of calcite:

$$CaCO_3 \rightarrow CaO + CO_2$$

or the oxidation of pyrite:

$$4 \operatorname{FeS}_2 + 11 \operatorname{O}_2 \rightarrow 2 \operatorname{Fe}_2 \operatorname{O}_3 + 8 \operatorname{SO}_2.$$

(The inorganic chemistry of coal is treated in Chapter 18.) Because of this, the weight of ash in the proximate analysis does not necessarily indicate the weight of inorganic material originally in the coal. For the most precise work, it would be preferable to express coal parameters not on an ash-free basis, but on a mineral-matter-free basis [E]. This implies having some method of determining the amount of inorganic material in the coal before it undergoes reaction. Doing this is not easy, and this was especially so before the availability of modern instrumental techniques, for which the instruments themselves

Class and group	Fixed carbon, % mmmf	Volatile matter, % mmmf	Heating value, Btu/lb, m,mmf
I. Anthracitic			
1. Metaanthracite	>98	<2	
2. Anthracite	92–98	2-8	
3. Semianthracite	86–92	8-14	
II. Bituminous			
1. Low volatile	78-86	14-22	
2. Medium volatile	69–78	22-31	
3. High volatile A	< 69	>31	> 14000
4. High volatile B			13 000-14 000
5. High volatile C			10 500-13 000
III. Subbituminous			
1. Subbituminous A			10 500-11 500
2. Subbituminous B			9500-10 500
3. Subbituminous C			8300-9500
IV. Lignitic			
1. Lignite A			6300-8300
2. Lignite B			< 6300

Table 17.1 The American Society of Testing and Materials system for classification of coals by rank.

are not inexpensive. Consequently, empirical relationships were developed to calculate the amount of mineral matter from the amount of ash. The Parr formula is expressed as

$$MM = 1.08 [A + 0.55 S],$$

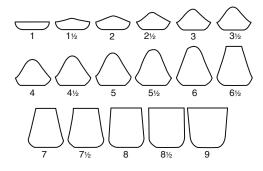
where MM is mineral matter; A, the ash value; and S, the sulfur content, all expressed on a weight-percent basis. Using the Parr formula to calculate mineral matter, the proximate analysis data can then be converted to a mineral-matter-free basis by calculations analogous to those shown previously.

The ASTM rank classification of coals is based on the volatile matter or fixed carbon reported on a moisture-and-mineral-matter-free (mmmf) basis, and on the calorific value reported on a moist, but mineral-matter-free, basis (m,mmf). The rank classification scheme is given in Table 17.1.

Some overlap in heating value exists between the subbituminous A and high volatile C classifications, specifically the range of 10 500–11 500 Btu/lb. Coals having heating values in this range are classified as high volatile C bituminous if they display caking properties (discussed in the next section), and as subbituminous A if they do not. Informally the class and group names are sometimes mixed; for example lignitic coals are often commonly referred to simply as lignites, with no distinction drawn between lignite A and lignite B. Lignites and subbituminous coals together are called low-rank coals, bituminous coals and anthracites, high-rank coals.

## 17.2 The caking behavior of bituminous coals

Heating coals in an inert atmosphere drives off various volatile pyrolysis products. When this experiment is done with low-rank coals, or with anthracites, the carbonaceous solid remaining is a powdery material that might look very much like the



**Figure 17.1** Chart used for assignment of free swelling index values for caking coals. The numbers correspond to the free swelling index value for the variously shaped coke "buttons." (This chart is not to exact scale and should not be used for assigning free swelling indices.)

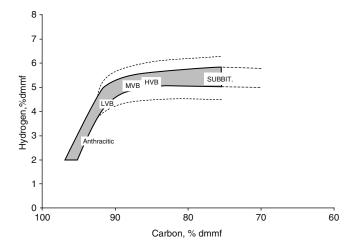
original, unheated sample. Not so with bituminous coals. With bituminous coals, the residue may appear to have fused into a single, solid mass. It may also appear not only to have fused, but to have softened and swollen into a much larger volume than the original sample. Coals that exhibit this behavior are called caking coals. Only coals of bituminous rank display caking behavior.

In the United States the caking behavior of coal is measured by the free swelling index (FSI). The FSI test uses a crucible of standard size, in which the sample of coal is heated at 820 °C for 2.5 min in an inert atmosphere. Comparing the size and shape of the resulting "button" with a series of standard outlines allows assigning a numerical value of FSI from 1 to 9. The FSI chart is illustrated in Figure 17.1. (The dimensions of this figure are not those of the ASTM standard, so *Figure 17.1 should not be used for FSI determination*.) If the heated sample does not form a coherent mass, but just falls apart when removed from the crucible, the assigned FSI is 0.

In practical coal technology, the caking behavior of bituminous coals plays a vital role in production of metallurgical coke. Chapter 23 discusses this behavior in more detail. The subset of the caking coals that leads to production of metallurgical coke is called the coking coals. All coking coals are necessarily caking coals, but not all caking coals can serve as coking coals.

## 17.3 Elemental composition

Determining the principal elements in coal – carbon, hydrogen, nitrogen, sulfur, and oxygen – is referred to as ultimate analysis. In this context, the word *ultimate* derives from an early usage in analytical chemistry, indicating determination of elemental components without regard to how they are arranged in the molecular structure. It is not ultimate in the sense of being "incapable of further analysis," since, at some level, every known element occurs in coal, excepting only the synthetic, highly radioactive elements and the noble gases. Customarily, only carbon, hydrogen, nitrogen, and sulfur are determined directly. Oxygen is then calculated from



**Figure 17.2** The Seyler coal band. Most humic coals have carbon and hydrogen contents within the region of this band. LVB is low-volatile bituminous; MVB, medium-volatile; HVB, high-volatile; and SUBBIT, subbituminous. Seyler's original data base did not extend to coals having less than about 75% carbon, so extension to coals of lower rank must be based on extrapolation.

## O = 100 - (C + H + N + S).

In this equation the elemental symbols refer to the percentage of the corresponding elements found in the sample. Unless explicitly stated otherwise, ultimate analysis data in this book are always on an mmmf or maf basis.

Despite wide variation in carbon contents across the rank range, the hydrogen content of humic coals is fairly constant at  $\approx 5.5\pm0.5\%$  up to a carbon content of  $\approx 88\%$ . The Seyler chart [F] represents the variation of hydrogen as a function of carbon, Figure 17.2. (The abscissa runs "backwards," in the sense that the origin is not at (0,0) but rather is at (100,0).)

Coals are sufficiently variable that it would be beyond hope to expect the data to fall all on a line; but the composition of most coals falls within the band shown on this chart. As originally constructed, the Seyler chart extended only to coals of >75% carbon. The dashed lines represent an extrapolation to coals of lower rank, although extrapolations must always be treated with caution [H]. Below  $\approx 88\%$  carbon, the hydrogen vs. carbon band has a slope of nearly zero. This suggests that, in the region below 88% carbon, coalification reactions have been dominated by loss of oxygen, rather than hydrogen, consistent with the van Krevelen diagram of Figure 8.10. The slope change at 88% carbon indicates a major shift in the reactions occurring during coalification, again consistent with the van Krevelen diagram. The point at the origin (100,0) is graphite, as would be expected from the hydrogen redistribution diagram (e.g. Figures 8.3–8.5). The Seyler chart applies only to humic coals, but these are the dominant coals in the world. Some unusual coals have formed from Type I or II kerogen, and can contain up to  $\approx 12\%$  hydrogen.

Figure 17.3 illustrates the variation of oxygen content with rank.

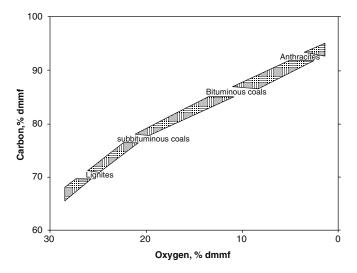
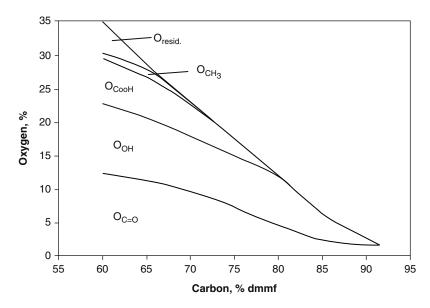


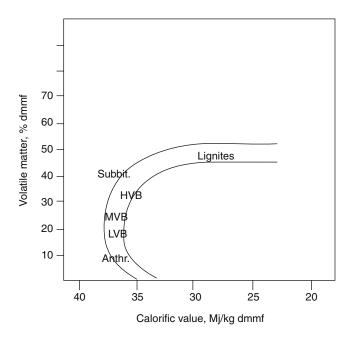
Figure 17.3 Relationship of oxygen content and carbon content for humic coals. Generally oxygen content decreases as rank increases.



**Figure 17.4** Relationship of oxygen functional group content to carbon content. Residual oxygen (O<sub>resid</sub>) may be present as various heterocyclic ethers.

Again the data plot in a band, not on a single line. The oxygen band approximates a straight line. Since hydrogen content varies little with rank, up to  $\approx 88\%$  carbon, the increase in carbon content with rank relates primarily to loss of oxygen. The data in Figure 17.3 also show that, for most coals, oxygen is the second most important element, expressed on a weight basis. Oxygen in coal reduces the heat of combustion; the same argument applies here as discussed earlier for ethanol.

The variation of oxygen functional groups with rank is shown in Figure 17.4.



**Figure 17.5** The Mott chart illustrates the relationship between calorific value and volatile matter. Most humic coals fall within the band. Subbit is subbituminous coal; HVB, high-volatile bituminous coal; MVB, medium-volatile; LVB, low-volatile; Anthr, anthracite.

The principal oxygen functional groups in coals are carboxylic acids, phenols, quinones, and ethers. These groups provide sites where reactions of the coal could occur. Other oxygen functional groups, such as esters, aliphatic alcohols, and aldehydes, have little importance and may be completely absent. Methoxyl groups are important only in low-rank coals. These groups derive from lignin. Their disappearance from coals above  $\approx$ 72% carbon suggests that lignin structures have been extensively converted by the time that coal has reached subbituminous rank. Carboxyl groups can retain inorganic cations in the coal. They vanish from coals above  $\approx$ 80% carbon, about the division between subbituminous A and high volatile C bituminous coals.

The Mott coal classification, also known as the Mott [G] chart, Figure 17.5, illustrates the variation of calorific value with rank.

Coals of highest calorific value are not the coals of highest rank. Among a series of fuels, heat of combustion, or calorific value, generally decreases with decreasing H/C ratio. As a rule, when the hydrogen content of a family of compounds drops, the heat of combustion *per mole of carbon* drops also. Table 17.2 provides some data that illustrate this behavior.

Natural gas, with H/C of 4.0, has a calorific value of  $\approx$ 56 MJ/kg. Many petroleum products with H/C about 2, have calorific values of  $\approx$ 46 MJ/kg. Taking an H/C of 0.75 for a "typical" coal, the extrapolated calorific value would be about 37 MJ/kg. Coals having H/C ratios of  $\approx$ 0.75 actually have calorific values of 28–32 MJ/kg on an mmmf basis. Coals of even the best quality seldom exceed 36 MJ/kg.

Compound	Atomic H/C	$\Delta H$ , kJ/mol	$\Delta H$ , kJ/mol C
Methane	4.00	-882	-882
Propane	2.67	-2203	-734
Decane	2.20	-6740	-674
Toluene	1.14	-3910	-559
Benzene	1.00	-3268	-545
Naphthalene	0.80	-5156	-516

**Table 17.2** Data showing the dependence of the heat of combustion per mole of carbon on the atomic H/C ratio for simple alkanes and aromatic hydrocarbons.

**Table 17.3** The variation of heat of combustion as a function of oxygen content for some selected oxygen-containing compounds.

Compound	Atomic O/C	% O	$\Delta H$ , kJ/mol	$\Delta H$ , kJ/mol carbon
Ethane	0	0	-1540	-770
Ethanol	0.50	35	-1373	-687
Ethylene glycol	1.00	52	-1180	-590
Propane	0	0	-2219	-740
1-Propanol	0.33	27	-2021	-674
Acetone	0.33	28	-1790	-597
Methyl acetate	0.67	43	-1592	-531
Benzene	0	0	-3268	-545
Phenol	0.17	17	-3054	-509
Benzoic acid	0.28	26	-3228	-461

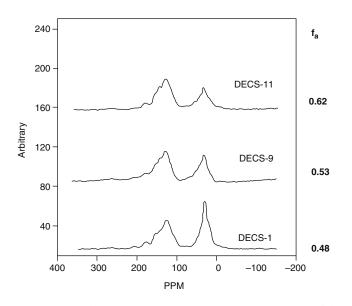
The discrepancy between the extrapolated and actual calorific value arises from two significant ways in which coals differ from natural gas and petroleum. First, most coals contain more oxygen than is found in natural gas or petroleum. Incorporating oxygen into an organic molecule reduces the heat of combustion, as shown in Table 17.3. Second, most of the carbon in coals is aromatic, not aliphatic as it is in natural gas and petroleum.

By inference, aromatic carbon should dominate in coals. For almost all coals, H/C < 1, typical of aromatic compounds. For example, naphthalene has an H/C ratio of 0.80, and chrysene, 0.67. Humic coals derive from Type III kerogen, dominated by lignin, which has a structure based on phenylpropane units. However, direct evidence can be obtained from carbon-13 nuclear magnetic resonance spectroscopy, which clearly shows the dominance of aromatic carbon in coal, see Figure 17.6.

The parameters used to characterize the aromatic structures in coal are aromaticity,  $f_a$ , and ring condensation, R. Aromaticity represents the fraction of the total amount of carbon incorporated in aromatic structures, i.e. the amount of aromatic carbon divided by the total amount of carbon. As one example, the aromaticity of butylbenzene,  $C_4H_9C_6H_5$ , is 0.60, i.e. six aromatic carbon atoms in ten total carbon atoms. Ring condensation is the average number of condensed rings in the aromatic units in a structure. Compound 17.1, for example, has two aromatic ring systems, one with two fused rings and the other with three. The ring condensation would be 2.5, i.e. (2 + 3)/2. Both  $f_a$  and R increase with increasing

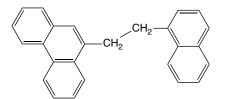
Compound	<b>Ring condensation</b>	Stabilization, kJ/mol carbon		
Benzene	1	25.1		
Naphthalene	2	31.4		
Phenanthrene	3	33.1		
Triphenylene	4	34.7		

**Table 17.4** Variation of resonance stabilization energy per carbon atom as a function of ring condensation for selected aromatic hydrocarbons.



**Figure 17.6** Carbon-13 nuclear magnetic resonance spectra of three low-rank coals, increasing from lignite to subbituminous coals. The increase in aromaticity,  $f_a$ , is reflected by the decrease in the aliphatic peak and increase in the aromatic carbon peak. The spectra are offset by an arbitrary amount for clarity of illustration.

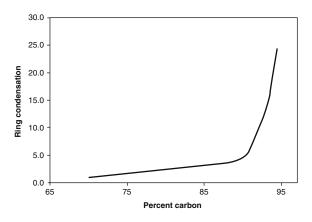
rank. Aromaticity appears to rise linearly with rank, from 0.6–0.7 for lignites to about 1 for anthracites. Ring condensation also rises monotonically with rank, see Figure 17.7, but with a relatively low slope from lignites ( $R \approx 1.5$ ) through the bituminous coals ( $R \leq 5.5$ ). However, beyond about 90% carbon, the slope becomes much steeper, rising to some 30–100 in anthracites, and being infinite (on an atomic scale) in graphite.



17.1 A compound illustrating ring condensation index of 2.5

Compound	Aromaticity, $f_a$	$\Delta H$ , kJ/mol	$\Delta H$ , kJ/mol carbon	
Decalin	0.00	6287	629	
Tetralin	0.60	5659	566	
Naphthalene	1.00	5157	516	

 Table 17.5 Effect of increasing aromaticity on the heat of combustion for a series of compounds of similar structure.



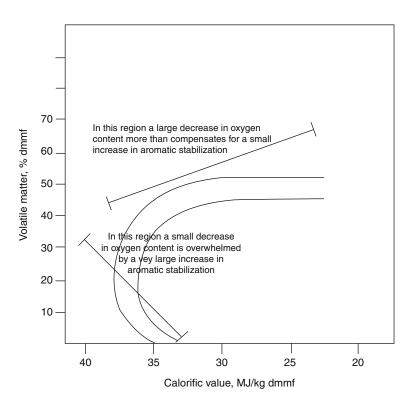
**Figure 17.7** The average ring condensation (i.e. number of condensed rings per aromatic unit) as a function of carbon content. Most humic coals are likely to lie in a band surrounding the line.

Consideration of heat of combustion of  $C_6$  cyclic compounds shows a linear decrease from cyclohexane to cyclohexene to cyclohexadiene. Extrapolation to cyclohexatriene, better known as benzene, shows that the actual heat of combustion is lower than the extrapolated value. This reflects the resonance stabilization of the aromatic benzene molecule. With increasing ring condensation, the resonance stabilization per carbon atom also increases, see Table 17.4. As a family of compounds becomes more aromatic, the heat of combustion per mole of carbon decreases, illustrated in Table 17.5. Furthermore, as the number of condensed rings increases, a drop in heat of combustion per mole of carbon occurs again, illustrated by the data in Table 17.6.

These two factors – oxygen and aromaticity – taken together explain the shape of the Mott chart. In the series from lignites to low-volatile bituminous, oxygen content drops from  $\approx 25\%$  to  $\approx 4\%$ . Over the same rank range, R increases from about 1.5 to about 5. These two effects work against each other, in that a decrease in oxygen content raises the calorific value, whereas an increase in ring condensation reduces it. But, over this range, the very large drop in oxygen more than compensates for the increase in ring condensation, so the net effect increases calorific value from lignite to low-volatile bituminous coal. From low-volatile bituminous coal to anthracite, the oxygen content decreases slightly, from  $\approx 4\%$  to  $\approx 2\%$ , but ring condensation increase greatly, from about five to somewhere over 30, possibly even over 100. Now, the increase in resonance stabilization energy as a function of increasing ring condensation, with a decrease in calorific value, overwhelms the small gain that comes from the relatively slight decrease in oxygen content. Figure 17.8 summarizes these effects.

**Table 17.6** Reduction in the heat of combustion per mole of carbon for a series of compounds of increasing ring condensation.

Compound	Number of fused rings	$\Delta H$ , kJ/mol	$\Delta H$ , kJ/mol carbon
Benzene	1	3275	576
Naphthalene	2	5157	516
Phenanthrene	3	7075	506
Chrysene	4	8954	497



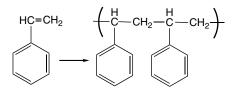
**Figure 17.8** A possible structural explanation for the variation observed in the Mott chart (Figure 17.5). As rank increases up to medium- to low-volatile bituminous, a large increase in calorific value due to the decrease in oxygen content outweighs the reduction in calorific value due to the increase in aromatization and ring condensation. In the highest rank range, increased aromatic ring condensation overwhelms the relatively small decrease in oxygen content, with a net decrease in calorific value.

# 17.4 The macromolecular structures of coals

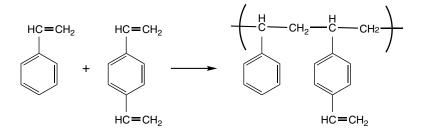
Coals do not have a unique molecular structure. This distinguishes coals from polymers, which have regular, repeating structures based on a monomer (sometimes two or three monomers) that have been well characterized. Coal is also distinct from biological macromolecules, which might have a very large and complex structure but, once it has been elucidated is then known unequivocally. In contrast, coal scientists studying "coal structure" work with so-called average structures, that are created to agree with the ultimate analysis, the distribution of functional groups,  $f_a$  and R, and perhaps other measured features, such as molecular weight distribution. These average structures are not believed to be *the* structure of coal, but rather are convenient illustrations to help explain the properties and reactions of the coal [H]. Progress continues to be made both in development of increasingly powerful analytical instruments for probing the structural features of coals and development of more powerful computational methods, capable of handling greater and greater numbers of carbon atoms in molecular models.

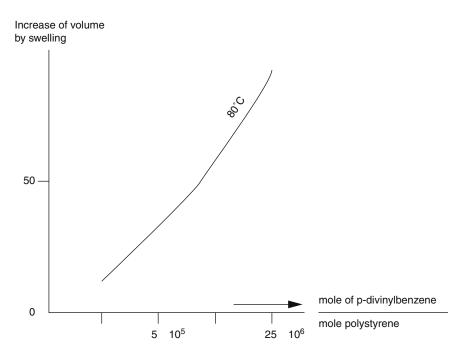
Coals can be considered as starting at one end with lignin, and winding up at the other end with graphite. The structure of lignin was discussed in Chapter 6. Lignin consists of the aromatic structures in its monomers, sinapyl, *p*-coumaryl, and coniferyl alcohols, linked through the  $C_3$  aliphatic units and through ether groups. Though most coals contain aromatic units larger than single-ring structures, they consist of aromatic structures connected by one or more methylene groups, and/or by hetero-atomic structures. Therefore, the lignin structure provides an analogy, albeit an approximate one, for the structures in coals. The aliphatic or heteroatomic links between aromatic structures are called crosslinks. Though coal cannot be spoken of as being a true polymer, concepts in polymer science – especially those of crosslinking and solvent swelling – can help in understanding the macromolecular structures of coals.

To illustrate the notion of crosslinking, styrene polymerization serves as a useful example. Styrene readily undergoes polymerization to the ubiquitous poly-styrene:



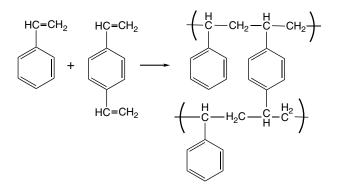
The polymer chains in this material interact via London forces and possibly  $\pi-\pi$  interactions between the aromatic rings. Polystyrene readily dissolves in a variety of common organic solvents, such as benzene or carbon tetrachloride. But, if a small amount, even 0.1%, of divinylbenzene is incorporated into the polymerization reaction, the initial product can be represented conceptually by





**Figure 17.9** The effect of crosslinking on solvent swelling, as shown for the co-polymer of divinylbenzene and styrene. As the amount of the crosslinking agent divinylbenzene increases, swelling decreases.

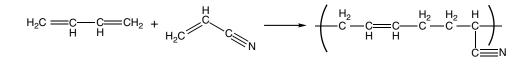
The double bond in the second vinyl group provides a site for further polymerization in a second polymer chain:



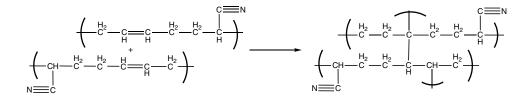
In this styrene: divinylbenzene copolymer the polymer chains are not linked by London forces, but rather are connected through covalent bonds in the divinylbenzene monomers. These linkages between polymer chains are called crosslinks. Such a copolymer cannot dissolve, because solvents cannot break covalent bonds. (If they did, this would not be dissolution but rather chemical reaction.) At most, the interaction of solvent molecules with segments of the polymer chain will cause the polymer to swell. Figure 17.9 shows how incorporation of divinylbenzene into polystyrene affects the solvent swelling. Less crosslinking results in greater swelling.

Sample	Carbon	Hydrogen	Oxygen	Aromaticity	Ring condensation
Coniferyl alcohol	66.7	6.7	26.7	0.60	1
<i>p</i> -Coumaryl alcohol	62.9	6.7	30.5	0.55	1
Sinapyl alcohol	72.0	6.7	21.3	0.67	1
Lignite	70	5.5	22	0.6	1.5

**Table 17.7** Comparison of the compositions of lignites with those of the lignin monomers. Carbon, hydrogen, and oxygen values are in weight percents; for lignites the values are on a dmmf basis.



Similarly, the reaction of 1,3-butadiene with acrylonitrile leaves at first a material that can undergo a second polymerization via the residual double bonds:



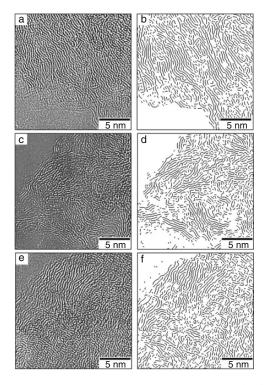
forming, as the resulting product, a three-dimensional, crosslinked polymer. This material, the co-polymer of 1,3-butadiene and acrylonitrile, called nitrile rubber, has numerous commercial applications that depend on its crosslinking, such as in the hoses on gasoline-dispensing pumps, where the rubber must resist any possible swelling or degradation – let alone dissolution – in the gasoline.

A polymer dissolves in two steps. First, solvent molecules diffuse into the polymer to produce a swollen gel; then the gel dissolves in the solvent to produce a true solution. With strong intermolecular forces between the polymer chains, e.g. hydrogen bonds or covalent crosslinks, solvent-polymer interactions are not adequate to overcome them. In that case, the process stops at the first step, leaving a swollen gel. Crosslinked polymers only swell when they interact with solvents. The extent to which such a polymer swells in a particular solvent indicates how extensively it is crosslinked. Swelling of coals exposed to organic solvents suggests that they can be considered as crosslinked structures.

Because lignin resists extensive degradation in diagenesis and early coalification, the macromolecular structure of lignites should resemble that of lignin: relatively small aromatic units joined by polymethylene and aliphatic ether crosslinks. Table 17.7 shows a comparison in compositions of the lignin monomers and samples of lignins and lignites.

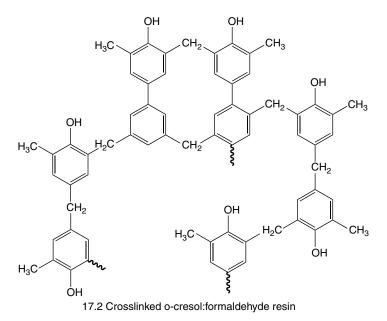
Similarities in composition are not proof of similarities in structure, but may be taken as circumstantial evidence that lignites bear chemical resemblance to lignin, and backwards from that into woody organic matter [I].

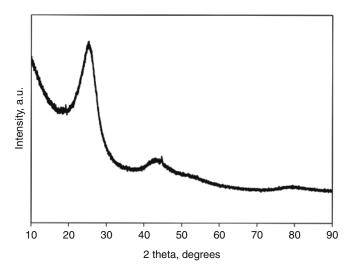
Highly crosslinked structures with small aromatic units and abundant oxygen functional groups also exist in resins produced from condensation polymerization of phenol



**Figure 17.10** Transmission electron micrograph of three Chinese anthracites, showing the structural ordering at the fine resolution of the microscope. From top to bottom, these anthracites are Si Wang Zhang, Men Tou Gou, and Guo Er Zhuang.

derivatives with formaldehyde. For example, reaction of *o*-cresol with formaldehyde leads to a structure like that depicted in structure 17.2 (the "squiggle" bonds in this structure indicate positions where the crosslinking continues).





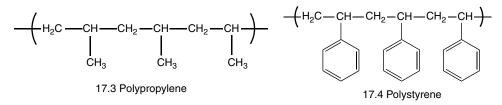
**Figure 17.11** An X-ray diffractogram of anthracite. The peak in the vicinity of 28° indicates the partially graphitic nature of the structure.

Similarly to lignites, these resins begin active thermal decomposition at temperatures  $\geq$  300 °C, and decompose without apparent evidence of softening. When such resins form with occluded water (the other reaction product from the condensation polymerization), the water gives rise to pores or "holes" in the macromolecular structure of the resin.

Compared to lignites, bituminous coals have higher carbon content, lower oxygen content, and higher values of  $f_a$  and R. Although the structure is still disordered on a molecular level, some evidence shows the beginnings of structural ordering in bituminous coals. For example, it is possible actually to see aromatic ring units beginning to align in some bituminous coals, using transmission electron microscopy.

Anthracites have carbon contents over 91%,  $f_a$  values  $\approx 1$ , and large values of R, likely to be in the tens or hundreds. Since graphite has  $f_a$  of 1.00 and R essentially infinite, anthracites approach the structure of graphite, albeit continuing to have some structural disorder. Figure 17.10 shows this. Particularly for high-rank coals and other materials with very high carbon contents, the X-ray diffractogram can be compared with that of graphite itself. Of particular interest is the very characteristic (002) peak, illustrated in Figure 17.11, for an anthracite and graphite.

Supporting evidence can be obtained by considering the properties of some simple polymers, such as polypropylene (17.3) and polystyrene (17.4).

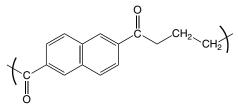


If samples of reasonably similar polymerization and crystallinity are compared, polystyrene has: higher density, tensile strength and flexural strength; lower solubility; a higher activation energy for flow in the melt phase; and higher viscosity in solution in



Figure 17.12 Marie Stopes, a pioneer of coal petrography and women's rights.

benzene. These changes in physical behavior agree qualitatively with what might be anticipated from introducing  $\pi$ - $\pi$  forces into the structure. Poly-(ethylene naphthalate), 17.5, differs from common poly (ethylene terephthalate) (often known as PET and widely used in soft-drink bottles) in that the aromatic units are based on naphthalene rather than benzene structures. Of the two, poly-(ethylene naphthalate) is much stronger, much higher melting, and less permeable to oxygen.



17.5 Poly(lethylene naphthalate)

Comparing pure aromatic compounds and polymers containing aromatic units suggests that increasing the number or size (or both) of aromatic ring systems in a material results in its becoming more dense, higher melting, less soluble, and physically stronger. The ultimate aromatic compound, and the end point of the carbon-rich series of materials, is graphite. Graphite is inert toward virtually all substances except under extreme reaction conditions. It is not soluble in any solvent. It scarcely oxidizes, even at white heat. Its melting point is about 3600 °C.

The solvent swelling behavior of various coals shows that the extent of crosslinking drops as rank increases from lignites up to about 88% carbon, near the upper end of the bituminous rank range. Since  $f_a$  and R also increase, it is likely that this behavior results from incorporation of aliphatic crosslinks into growing aromatic ring systems. The apparent extent of crosslinking then increases from  $\approx 88\%$  carbon into the anthracites. While some covalent crosslinks (such as aromatic ethers) may exist in anthracites, the other significant factor with very large values of R is the possibility of  $\pi$ - $\pi$  interactions. In graphite, both electron delocalization and van der Waals effects contribute to the interlayer interactions.

## 17.5 Coals as heterogeneous solids

Transformation of kerogen to natural gas or petroleum results in homogeneous fluids. Their appearance on a microscopic or macroscopic level provides no distinctions that can be related to the original kerogen source material. But, because of coals being

Lithotype	Color	Appearance	Fracture
Vitrain	glossy black	narrow bands	conchoidal
Clarain	black	lenticular	breaks to glassy surface
Durain	dull gray-black	lenticular	fine-grained
Fusain	charcoal-like	small lenticular	friable, breaks to powder

solids, physical mixing or mutual solubility of the components does not occur. This makes it possible to discern microscopic regions in the coal that clearly relate to the original organic matter.

In geology, a rock is a solid material that is an aggregate of individual minerals (usually two or more kinds) in various proportions. Granite provides an example. Examining granite under a microscope, sometimes even by the unaided eye, shows that it consists of individual grains or particles, which are the mineral components of the rock. Similarly, examining coal under a microscope reveals its individual components. Coal can be considered to be an organic rock; its individual components, the "organic minerals," are called macerals.

Description and classification of macerals from their optical appearance and relationship to botanical structures in the original organic matter forms the basis of the field of coal petrography. The foundations of this discipline were established in the 1920s by Marie Stopes [J], see Figure 17.12.

Macerals derive from different components of the original plant material that eventually produced that specific sample of coal. Different plant components have different molecular structures – lignin and wax, for example. Substances with different molecular structures undergo different kinds of chemical reaction at a given set of conditions, or participate in a given chemical reaction in different ways. Though plant components experience chemical alteration during diagenesis and catagensis, macerals still reflect the chemical and botanical differences inherent in the original organic matter. These differences between the macerals, consequently, result in differences in their chemical behavior. By knowing the relative proportions of the macerals in a coal sample, which can be determined by optical microscopy, it becomes possible to make some predictions about its behavior and reactivity.

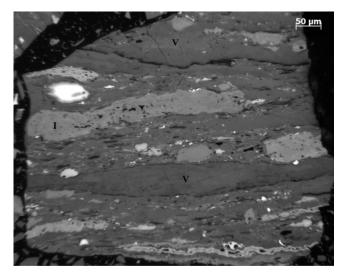
Particularly with bituminous coals, it is often possible to discern regions of distinct appearance, i.e. bands, even with the unaided eye. These bands are called lithotypes, usually distinguished by appearance and fracture, Table 17.8.

Lithotype shows are made of smaller constituents, the macerals. Macerals are classified into groups, summarized in Table 17.9.

Vitrinites predominate among the macerals of most northern hemisphere coals, see Figures 17.13–17.15. For that reason, and because of their good chemical reactivity, many fundamental studies in coal chemistry focus on vitrinite. Vitrinite, fusinite, and semifusinite are likely to derive from wood or bark. Liptinites or exinites form from plant debris such as resins, spores, pollen grains, or leaf cuticles, and from algae. Some coals in Utah in the United States contain large blocks of resinite that can be picked by hand from the coal. Coals with a large amount of cutinite include the unusual "paper coals" of the United States (Indiana) and Russia. Alginite occurs in large amounts in algal coals of Scotland and Tasmania, the torbanites and coorongites. Inertinite macerals derive their name because they are relatively inert during coke-making. However, "reactive

Maceral group	Appearance	Composition	Example macerals	Plant origin
Vitrinites	shiny, glass- like	oxygen-rich moderate hydrogen moderately aromatic	tellinite collinite	wood or bark gelified humic material
Exinites	waxy or resinous	hydrogen-rich highly aliphatic	alginite cutinite resinite sporinite	algal remains leaf cuticles resins spores
Inertinites	dull, charcoal- like	carbon-rich highly aromatic	fusinite semifusinite sclerotinite	carbonized or degraded wood fungal remains

Table 17.9 Properties of the maceral groups, and examples of specific macerals in each group.

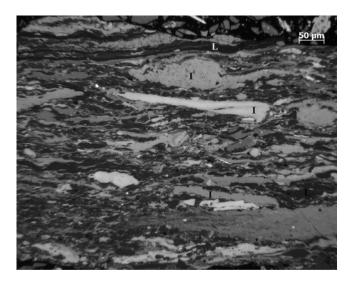


**Figure 17.13** A photomicrograph of a high volatile A bituminous coal showing high and low reflecting inertinite macerals (I) contained in a vitrinite (V) matrix.

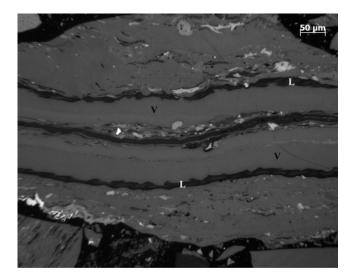
inertinites" are very important in coals of South Africa. Fusinite and semifusinite represent "fossil charcoals;" other inertinites, such as sclerotinite, may be remains of fungal attack on wood. The apparent density varies as inertinites > vitrinites > liptinites.

# 17.6 Physical properties

Density is usually measured by displacement of a fluid. Because coals are porous, their apparent density depends on the fluid used for the measurement, particularly on the ability of the fluid molecules to penetrate the pore system. Apparent density is useful in engineering calculations, e.g. to size reactor vessels needed to contain a given quantity



**Figure 17.14** A photomicrograph of the same coal as in Figure 17.13, showing a coal layer composed largely of inertinite (I) and liptinite (L) group macerals with a lower concentration of vitrinite (see lower right hand corner).

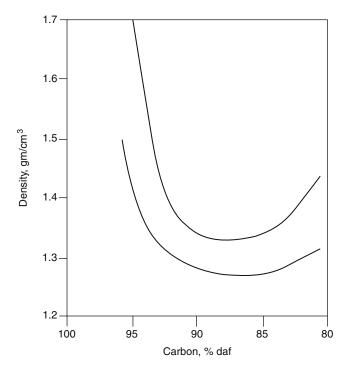


**Figure 17.15** A third photomicrograph of the same coal, in this case showing thick bands of a liptinite (L), namely cutinite, trapped in a uniform vitrinite (V) matrix.

of coal. Figure 17.16 shows the variation of apparent density, measured in methanol, as a function of carbon content.

Other liquids give curves of similar shape but displaced on the ordinate. Regardless of the liquid used, a broad minimum occurs in the range 85–90% carbon.

The so-called true density is measured by displacement of helium. The name "true density" derives from the assumption that helium, being the smallest atom, should be able to penetrate even the smallest of pores, whereas other fluids might not be able to



**Figure 17.16** The apparent density of coals as a function of carbon content, measured by displacement of benzene, hexane, methanol, or water. The densities of most coals lie within the band.

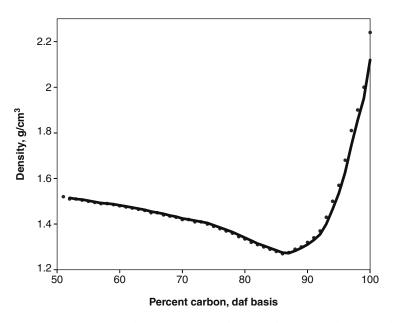


Figure 17.17 The helium density, or "true" density, of coals as a function of carbon content.

Compound	Aromaticity, $f_a$	<b>Ring condensation</b>	Density, g/cm <sup>3</sup>	
2-Ethylnaphthalene	0.83	2	1.008	
9-Ethylanthracene	0.88	3	1.041	
2-Methylnaphthalene	0.91	2	1.029	
9-Methylanthracene	0.93	3	1.066	
Naphthalene	1	2	1.145	
Anthracene	1	3	1.250	
Chrysene	1	4	1.274	
Coronene	1	7	1.371	
Graphite	1	$\infty$	2.25	

**Table 17.10** Densities of selected simple aromatic molecules, indicating increased density as structure becomes more aromatic and compact.

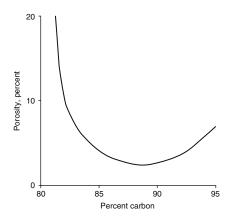


Figure 17.18 The porosities of coals as a function of carbon content.

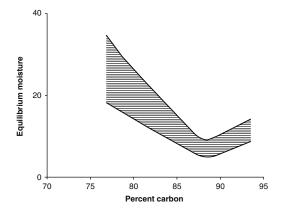
penetrate all of the pore system of the sample. The alternative name is helium density. It varies with carbon content as shown in Figure 17.17.

For coals below  $\approx 88\%$  carbon, the variation of helium density reflects the effect of decreasing oxygen content; above 88% carbon, the variation indicates increasing structural order. The trends for simple aromatic molecules, Table 17.10, illustrate this.

Bulk density depends on the volume occupied by a given mass of coal lumps or particles. Bulk density varies with particle size and packing efficiency of the particles. It conveys no fundamental information about the structure and properties of coals, but has use in estimating the weight of coal that could be held in, e.g. storage bins, trucks, or railway cars.

Porosity varies with rank as shown in Figure 17.18.

Since surface area controls the extent and rate of heterogeneous reactions, in many applications knowledge of total surface area is more important than knowing the porosity. Surface area measurements are commonly made by gas adsorption. The concepts of surface area and porosity measurements have importance not only in coal reactivity, but also in the fields of heterogeneous catalysis (Chapter 13) and the characterization of carbon products made from fossil and biofuels (Chapter 24).

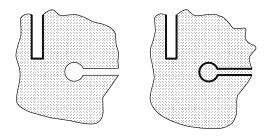


**Figure 17.19** The equilibrium moisture of coals as a function of carbon content. Most coals lie within the shaded band. The trend generally follows that of porosity, as shown in Figure 17.18.

The total surface area of a particle is composed of the external surface of the particles plus the internal surfaces on the walls of pores. In lignites, the internal surfaces contribute about 90% of the total surface area. Lignites have surface areas of  $\approx 200 \text{ m}^2/\text{g}$  when measured by adsorption of carbon dioxide. Because of the ability of pores to fill with water, the moisture content of lignites determined by proximate analysis can be 35–45%. An estimate of the amount of pore volume could be determined from the moisture content *if* it were certain that the pores were full and no extraneous moisture were present on the surface. This can be done by saturating the coal with water and storing the wet coal at 100% relative humidity until it comes to a constant weight. At that point, the moisture in the coal is held entirely in the pore system, and is referred to as the equilibrium moisture content. Equilibrium moisture varies from coal to coal, even among coals of the same rank. Lignites have the highest equilibrium moisture values of any rank of coal, in the range 20–40%. Figure 17.19 shows the variation of equilibrium moisture with rank.

With the highest surface area and highest porosity, lignites are generally very reactive coals. (But, in addition, lignite reactivity is also affected by the abundance of many kinds of functional groups, and comparatively low values of aromaticity and ring condensation.) Bituminous coals have lower porosities and total surface areas than lignites; with identical reagents and reaction conditions, bituminous coals are likely to be less reactive than lignites. Anthracites are slightly more porous than the bituminous coals. The aliphatic crosslinks in bituminous coals can exist in various conformations that may allow for closer filling of space than can be achieved with the very large aromatic ring systems ( $R \approx 10-100$ ) connected by short, rigid crosslinks characteristic of anthracites.

By knowing the surface area and pore volume, and by making an assumption about the shapes of the pores, the average pore radius can be calculated. This gives an idea of the sizes of molecules that can penetrate or leave the pore system. Gases commonly used for surface area measurements are carbon dioxide and nitrogen. Results obtained on the same sample depend greatly on the gas used: values measured by  $CO_2$  adsorption can be one or two orders of magnitude higher than those measured using N<sub>2</sub>. This large



**Figure 17.20** "Ink-bottle" pores are those having a narrow neck opening into a larger interior cavity, as shown horizontally in the sketches in this figure. An adsorbent not capable of penetrating the narrow pore neck will penetrate only the straight-walled pore, as indicated with heavy lines in the pore shown in the left-hand sketch. An adsorbent capable of penetrating both kinds of pore will fill both, indicated with heavy lines of both pores in the right-hand sketch. In the latter case the measured apparent surface area is higher.

discrepancy results from the diffusion of gases being an activated process, i.e. is temperature-dependent.  $CO_2$  adsorption is done at temperatures up to 25 °C, while N<sub>2</sub> adsorption might be done at -185 °C. This temperature difference could result in more rapid diffusion and equilibration of  $CO_2$  relative to N<sub>2</sub>. Activated diffusion would be especially important for so-called ink-bottle pores, see Figure 17.20, for which N<sub>2</sub> diffusion through the restricted opening would be very difficult at -185 °C, but much easier for  $CO_2$  at 25 °C. Because the value of measured surface area depends on the gas used as the adsorptive, there is no uniquely defined surface area of a porous solid such as coal. Measured surface area depends on the way the adsorbent (i.e. the coal) behaves in the experiment, and on the specific experimental conditions. Reporting the numerical value of surface area without indicating the adsorptive used is meaningless.

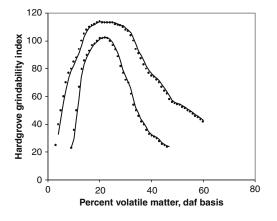
Mining procedures generally produce large lumps of coal, far larger than can be accommodated or effectively used in utilization processes. The hardness of coal, and its susceptibility to breaking, are important properties in transportation and handling of coal, as well as in size reduction operations prior to its use. Friability expresses the tendency of coal to break. In the drop shatter test, a sample is allowed to fall 2 m onto a steel plate. The size stability, S, is calculated as the ratio of average particle size after the test, Y, to average particle size of the original sample, X. Thus,

$$S = 100 (Y/X).$$

Friability is then calculated as

$$F = 100 S.$$

Grindability indicates how easy it is to grind coal to a specified size distribution, from a larger size distribution of the feed. The Hardgrove grindability index, HGI, was developed in the 1930s to assess grinding of coals for feeding to a pulverized-coal-fired boiler. In this test, a sample of specified particle size range is put into a bowl in which eight steel balls can run in a circular pathway. A ring is placed on top of the grinding balls, to put a specified weight on the balls. The apparatus is operated through 50 revolutions. At the end of the test the value of HGI is determined from the weight of <74  $\mu$ m particles. For an easy-to-grind bituminous coal HGI is 100. The Hardgrove grindability index varies with rank in a way similar to many other coal properties,



**Figure 17.21** The variation of Hardgrove grindability index of coals as a function of rank, expressed as volatile matter content.

showing a distinct slope change in the bituminous range when grindability is plotted as a function of rank. Figure 17.21 illustrates the rank variation of HGI as a function of volatile matter content.

Moisture content affects grindability; usually a range of values is reported for a given coal.

#### Notes

- [A] The operative term here is "in principle." Even with modern organic analytical instrumentation, determining and identifying every component in a sample of petroleum would be a formidable undertaking, not for the faint of heart. In the era when mixtures were separated by distillation, fractional crystallization, or open-column chromatography, and compounds were identified by such physical properties as melting point or refractive index, decades could be spent isolating and identifying a few hundred compounds from one sample of petroleum.
- [B] While the ASTM classification system is widely used, it is by no means universally adopted. Other standards-setting bodies, including the International Organization for Standardization (ISO), British Standards Institution (BS or BSI), the Deutsches Institut für Normung in Germany (DIN), and the Standards Committee in Poland (PN), have issued standards for classification of coals. And, there are others. While there do not seem to be radical differences between these systems, for precise work it is important to find out which system is being used (i.e. whose rules are we playing by?) for classification.
- [C] As an example, before the development of cryogenic techniques, gases that were difficult to liquefy, such as oxygen and nitrogen, were known as "fixed gases."
- [D] Proximate analysis is not confined to coal chemistry. Water hardness is sometimes reported in units of "parts per million calcium carbonate" regardless of which specific cations and anions contribute to the hardness of that particular sample. When we have blood tested as part of a physical examination, the content of the

sometimes-ominous "triglycerides" is reported, a number that incorporates all of the various fat or oil molecules without identifying each specific fat or oil, let alone the fatty acid components of each.

- [E] Not all inorganic components of coals, especially of low-rank coals, are grains of minerals. Some occur as cations associated with the carboxylate groups, and others may occur in ill-defined ways as coordination complexes with heteroatomic functional groups. Much of the developmental work on finding ways to express coal composition on a "mineral-matter-free" basis involved bituminous coals, where counterions to carboxylate groups or coordination complexes are negligible. Thus it is common to speak of a "mineral-matter-free" basis as if all of the inorganic components were truly minerals.
- [F] This chart was developed by Clarence Seyler (1866–1959). He enjoyed a long and illustrious career in coal research, mostly spent in Wales. In 1942 he was named general consultant to the British Coal Utilization Research Association, and in 1955 was elected first president of the International Committee on Coal Petrology. One of Seyler's preferred ways of relaxing from his research was to investigate the origins of some of the delightful place-names around Swansea, such as Ystumllwynarth and Seinhenyd.
- [G] R.A. Mott made numerous contributions to coal science and technology in the mid-twentieth century. His book, *The Cleaning of Coal*, co-authored with W.R. Chapman, is a classic in the coal literature. Mott was also a keen historian, with special interest in the Industrial Revolution in Britain, particularly the development of the iron industry, which he traced back to 1640. In that field, his biography of Henry Cort, inventor of a process for making wrought iron, is the standard.
- [H] An average structure of a particular coal could be useful in, e.g., assessing the likely outcomes of various reactions tried with that coal, to predict what kinds of bond must be broken or functional groups removed, even though the average structure itself does not exist. As an analogy, we know that the solar system model of the distribution of electrons in atoms is not an accurate depiction of atomic structure, yet there is probably no better way to illustrate how a sodium atom and a chlorine atom interact to give sodium and chloride ions in salt.
- [I] Two of the greatest thinkers of the nineteenth century held diametrically opposed views on the usefulness of circumstantial evidence. Henry David Thoreau pointed out that, "Some circumstantial evidence is very strong, as when you find a trout in the milk." But in contrast, Sherlock Holmes warns that, "Circumstantial evidence is a very tricky thing. It may seem to point very straight to one thing, but if you shift your own point of view a little, you may find it pointing in an equally uncompromising manner to something entirely different."
- [J] Marie Stopes (1880–1958), a Scot educated at University College in London, is one of the most remarkable figures in fuel chemistry. Her formal training was in paleobotany. She studied coals to help test ideas that Earth at one time had a single super-continent. To get specimens from as far afield as possible, she lobbied Robert Scott to be allowed to join his expedition to Antarctica. Fortunately for both coal science and for women's rights, she was not taken along; Scott and all his men perished. In the 1920s and beyond, Stopes campaigned for women's rights, sex education, and family planning, the latter topics being virtually taboo for public

discussion in that era. While laying the foundations of coal petrology, at the same time she opened the first family-planning clinic in the United Kingdom. Sadly, her reputation has been tarnished by her advocacy of eugenics, and publicly expressing admiration for the views of Adolf Hitler.

#### **Recommended reading**

- Berkowitz, Nobert. *An Introduction to Coal Technology*. Academic Press: New York, 1984. An excellent introduction to coal and ways of using it. Several of the early chapters discuss aspects of coal composition, structure, and properties.
- Given, Peter H. An essay on the organic geochemistry of coal. In: *Coal Science, Volume III* (Gorbaty, Martin L., Larsen, Jown W., and Wender, Irving, Eds.) Academic Press: Orlando, 1984; pp. 65–252. A wide-ranging discourse on coal origins, structure, and composition, by one of the great coal scientists of the mid- to late-twentieth century.
- Miller, Bruce G. *Clean Coal Engineering Technology*. Butterworth-Heinemann, Burlington, MA, 2011. The most up-to-date review of clean coal technology; Chapter 2 reviews chemical and physical properties of coals.
- Nomura, Masakatsu, Kidena, Koh, Murata, Satoru, Yoshida, Shuhei, and Nomura, Seiji. Molecular structure and thermoplastic properties of coal. In: *Structure and Thermoplasticity of Coal.* (Komaki, Ikuo, Itagaki, Shozo, and Miura, Takatoshi, Eds.) Nova Science Publishers: New York, 2005; Chapter 1. This chapters covers relatively few coals, but illustrates approaches to studying coal structure utilizing modern instrumental and wet chemical techniques.
- Smith, K. Lee, Smoot, L. Douglas, Fletcher, Thomas H., and Pugmire, Ronald J. *The Structure and Reaction Processes of Coal*. Plenum Press: New York, 1994. Chapters 3 and 4 discuss coal geochemistry, macromolecular structure, and various instrumental techniques for studying coal structure.
- Van Krevelen, D.W. *Coal: Typology Physics Chemistry Constitution*. Elsevier: Amsterdam, 1993. This is the best single book on coal science, by the person who was possibly the greatest of the coal scientists.

In contrast to natural gas and petroleum, coals contain appreciable amounts of inorganic material. In extreme cases, the ash value from the proximate analysis can be in the range 30 to 40%. The ash yields from coal require provisions for collecting it from combustion systems and making arrangements for its disposal in an environmentally acceptable manner. The inorganic components of coals also impact the operation of combustion and gasification units.

Ash results from various reactions among the inorganic constituents of coal, which occur when the coal is burned or gasified. The inorganic constituents include mineral grains, cations associated with carboxylic acid groups, and other cations held in coordination complexes with various heteroatoms in the coal structure. *Mineral matter* refers to distinct grains of inorganic substances, such as quartz or clay, incorporated as a separate, distinct phase, usually of defined composition and structure.

While it is easy and convenient to correct analytical data to an ash-free (or moistureand-ash-free) basis, a more accurate correction is to a mineral-matter-free basis. This is because the weight of ash collected does not necessarily equal the total weight of inorganic constituents in the coal, because of the reactions that occur during ashing. As examples:

Dehydration:	$FeSO_4 \cdot nH_2O \rightarrow FeSO_4 + n H_2O$ ,
Oxidation:	$FeS_2 + 3 O_2 \rightarrow FeSO_4 + SO_2$ ,
Decomposition:	$CaCO_3 \rightarrow CaO + CO_2$ ,
Sulfur capture:	$CaO + SO_2 + \sqrt[1]{2} O_2 \rightarrow CaSO_4.$

The magnitude of the difference between the weight of ash and the weight of the original inorganic constituents of the coal depends on the contribution that each of these reactions makes during ash formation. Oxidation of pyrite,  $FeS_2$ , results in a weight gain, whereas decomposition of calcite,  $CaCO_3$ , results in a weight loss. Two coals giving the same ash yield in the proximate analysis do not necessarily have identical amounts of original inorganic constituents.

The Parr formula (Chapter 17) is the most widely used empirical method for calculating the mineral matter content from the ash yield. Several direct experimental methods have been developed in recent decades. Low-temperature ashing involves removal of the carbonaceous part of the coal in an oxygen plasma at  $\approx 150^{\circ}$ C, a reaction that can take weeks to go to completion. In principle, reaction at this low a temperature does not thermally alter any of the inorganic components of the coal, so the weight of the low-temperature ash should be very close to that of the original inorganic components. Further, the minerals found by analysis of the low-temperature ash (by X-ray diffraction, for example) are generally assumed to be those minerals that were indeed originally in the coal. The principal exception is bassinite,  $CaSO_4 \cdot \frac{1}{2}H_2O$ , formed by partial dehydration of gypsum,  $CaSO_4 \cdot 2H_2O$ . Computer-controlled scanning electron microscopy (CCSEM) is also very useful in identifying minerals in coal. It involves direct electron-microscopic observation of mineral grains and their identification based on composition. Because hundreds, even thousands, of individual mineral grains are analyzed and sized during the CCSEM procedure, the output includes not only the identification of minerals occurring in that particular sample, but also measurements of the total quantity of minerals and their distribution among various size fractions.

# 18.1 The origin of inorganic components in coals

Inorganic components come from three sources. The first is original plant material. Virtually all plants contain some inorganic material, especially wood, a main contributor to Type III kerogen. Some plants actively concentrate inorganic species in accumulations known as phytoliths. An example is the scouring rush (*Equisetum hyemale*), also known as the bottlebrush. Its common name derives from its ability to concentrate abrasive silica in phytoliths; thanks to this, a handful of scouring rush stems can be very effective in cleaning pots and pans. The scouring rush is a descendant of the plants that grew extensively in the coal swamps some three hundred million years ago.

Transport of minerals into the swamp while the plant debris was accumulating and undergoing diagenesis is a second source. Minerals accumulated in this way are called syngenetic. Silts in the swampy environment can mix with the accumulating and coalifying organic matter. Mineral grains – clays and quartz in particular – can be washed into the organic matter with water flowing through the swamp. As the water stagnates, the minerals settle into the organic matter. These minerals probably came from erosion or weathering of rocks in the surrounding countryside. Wind sometimes transports mineral grains – volcanic ash being an example – into the coal swamp.

After the coal seam has formed, water percolating through cracks and fissures in the coal can precipitate mineral grains into the coal. Ion-exchange processes can occur between the aqueous phase and functional groups in the coal. This represents a third source of inorganic components, called epigenetic minerals. Pyrite sometimes accumulates in coals in this way.

#### 18.2 Inorganic composition of coals

Most of the information available on the inorganic composition of coals derives from analysis of ashes. Continuing a tradition inherited from analysis of geological samples, elemental composition is reported in terms of the oxides of the major elements present, i.e.  $SiO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$ ,  $TiO_2$ , CaO, MgO,  $P_2O_5$ ,  $K_2O$ , Na<sub>2</sub>O, and SO<sub>3</sub>. (Sometimes the analysis report is normalized to an "SO<sub>3</sub>-free" basis; the usual clue that this has been done is the absence of SO<sub>3</sub> from the analysis report.) While it is possible that a few of these elements may exist in ash, at least in part, as their oxides, others, such as the alkali

oxides and oxides of sulfur and phosphorus, certainly do not. Further, elements such as silicon and aluminum might exist in part as their oxides, and in part in other forms, e.g. as aluminosilicate minerals. Much good work has been done in developing empirical correlations of ash composition as oxides with various manifestations of ash behavior in practical coal utilization processes. Unfortunately, such correlations cannot be pushed further to a fundamental level, because many of the species listed as oxides do not occur as such in the ash.

The way in which each element is distributed among possible modes of occurrence in a coal is also important regarding how the various elements behave when the coal is utilized. The way in which a given inorganic element is incorporated in a coal could be any of these: in solution in the water filling pores; associated with carboxylate groups as the counterion; as coordination complexes with heteroatoms; or as discrete mineral grains. A given element can occur in the same coal in more than one way. For example, a portion of potassium might be present as potassium carboxylates, and the remainder incorporated in clay minerals.

Metal carboxylates are important in coals only up to about 80% carbon (Figure 17.4), i.e. the low-rank coals. Carboxylate groups act as ion-exchange sites to accumulate cations from water percolating through the coal. Cations of the alkali and alkaline earth elements accumulate in this way. Generally, 90-100% of the sodium, 75–90% of the magnesium, 50–75% of the calcium, and 35–50% of the potassium present in low-rank coals can be associated with the carboxyl groups. Most of the remaining calcium and magnesium are present as carbonates, and potassium is present, in clays. Metal coordination compounds are poorly characterized and poorly understood. Chlorophyll provides an example of a coordination compound in living plants, and nickel and vanadium porphyrins, in oils. Possibly coordination compounds from the original plant matter could have survived diagenesis and have been incorporated in the coal, or may have formed during diagenesis and coalification. Metal carboxylates and coordination compounds are sometimes loosely, but quite incorrectly, called organometallic compounds. Actual organometallic compounds contain direct metalto-carbon bonds [A]. There seems to be no credible evidence for the presence of true organometallic compounds in coals.

Studying the distribution of elements among their possible modes of occurrence in coals involves sequential leaching of the coal sample and analysis of the leachate and/or residue. This approach is known broadly as chemical fractionation, for which laboratories have developed various procedures that differ in details, but have a generally consistent approach [B]. Chemical fractionation begins with a mild reagent, such as aqueous ammonium acetate, which removes elements present as counterions to carboxylate groups, i.e. present on ion-exchange sites. A second treatment, using a reagent such as dilute hydrochloric acid, dissolves carbonates, some oxides, and hydrous oxides, and possibly some elements present as coordination complexes. A third treatment, with hydrofluoric acid, removes silicates. Elements remaining in the residue after the third treatment are considered present in the coal as pyrite.

Aside from the inorganic material contributed by the original plant matter, generally a minor portion of the total, the ions, coordination compounds, and minerals present in a given sample of coal reflect whatever processes happened during syngenetic and epigenetic mineralization. The amount and composition of inorganic components in coals depend on highly variable factors, such as the environment of deposition of the original organic matter, the kinds of mineral that were carried into the coalifying plant matter, the inorganic components of water percolating through the coal, and on the geology of the surrounding countryside. Consequently, great variability exists in the inorganic content and composition of coals – not only coals in general or coals of a specific rank, but even among samples of a coal taken from different locations in one seam. For example, the lignites of the Great Plains region of North America show as much variability within a given seam as they do from one seam to another. As a result, coals of identical rank can have very different inorganic compositions, as well as different ash values.

Adventitious mixing of coal with rocks or minerals from strata immediately above or below the coal seam, or inter-seam partings, further complicates the situation. These inorganic components are not, and were not, part of the coal itself, but became incorporated in the "as-mined" coal during the mining process. Their composition depends on the local geology of the mine; the extent of their incorporation in as-mined coal depends on the details of the mining process and how much care was taken to avoid this happening.

A consequence of this variability is that generalizations about the inorganic composition are necessarily broad. Low-rank coals contain appreciable numbers of carboxylic ion-exchange sites that incorporate alkali and alkaline earth cations. Since carboxylic acid groups are important only in low-rank coals, such coals tend to have proportionately more sodium, potassium, calcium, and magnesium than do the bituminous coals and anthracites. Carboxylic acid groups do not occur in bituminous coals and anthracites, so in these coals the principal inorganic elements are silicon, aluminum, and iron. The amount of pyrite seems to increase with increasing rank, at least through the bituminous coals.

Coals accumulate, at least at trace level, almost every known element, except the short-lived, highly radioactive ones prepared in nuclear processes and the noble gases. Most are present only at the parts-per-million level. Some of the trace inorganic constituents are of great concern because of their possible negative effects on human health or on the environment. Mercury attracts particular attention in this regard. Arsenic, selenium, and cadmium are examples of other elements that could cause serious problems if released to the environment. Some trace elements, such as gallium and germanium, have important commercial uses in the pure state, and could be quite valuable. In principle, coal ash could be a source of such valuable elements [C]. A power plant burning 10<sup>4</sup> tonnes per day of a coal with an ash value of 10% would produce 1 kg/day of a trace element present at a level of 1 ppm in the ash. Over the years many processes for extracting useful trace elements have been tested in the laboratory or pilot plants, but none seems to have been commercialized. Extracting and concentrating elements occurring at such low levels is not a simple job; doing it with a process that can also make money is even harder.

# **18.3** Minerals in coals and their reactions

At least 125 minerals have been identified in coals. A third of these are listed in Table 18.1.

Mineral	Formula	Mineral	Formula
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>	Kieserite	MgSO <sub>4</sub> ·H <sub>2</sub> O
Ankerite	$CaFe(CO_3)_2$	Kyanite	$Al_2SiO_7$
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	Limonite	Fe <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O
Apatite	$Ca_5F(PO_4)_3$	Magnetite	Fe <sub>3</sub> O <sub>4</sub>
Aragonite	CaCO <sub>3</sub>	Marcasite	FeS <sub>2</sub>
Augite	(Ca,Na) (Mg,Fe,Al,Ti) (Si,Al) <sub>2</sub> O <sub>6</sub>	Melanterite	FeSO <sub>4</sub> ·7H <sub>2</sub> O
Barite	BaSO <sub>4</sub>	Melnikovite	$Fe(As,Fe)S_3$
Biotite	$(Mg, Fe)_6Al_2Si_6O_{21} \cdot 4H_2O$	Mirahilite	$Na_2SO_4$ ·10 $H_2O$
Bischofite	MgCl <sub>2</sub> ·6H <sub>2</sub> O	Mispickel	FeS <sub>2</sub> ·FeAs <sub>2</sub>
Calcite	CaCO <sub>3</sub>	Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2$
Chalcopyrite	CuFeS <sub>2</sub>	Muscovite	KAl <sub>3</sub> Si <sub>3</sub> O <sub>11</sub> ·H <sub>2</sub> O
Chlorite	(Fe,Mg) <sub>10</sub> Al <sub>4</sub> Si <sub>7</sub> O <sub>30</sub> ·15H <sub>2</sub> O	Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>
Diaspore	Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	Pyrite	FeS <sub>2</sub>
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	Pyyrhotite	$FeS_x$
Epidote	Ca4(Al,Fe)3Si6O25·H2O	Quartz	SiO <sub>2</sub>
Evansite	Al <sub>3</sub> PO <sub>7</sub> ·9H <sub>2</sub> O	Rutile	TiO <sub>2</sub>
Galena	PbS	Sanidine	KAlSi <sub>3</sub> O <sub>8</sub>
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	Siderite	FeCO <sub>3</sub>
Halite	NaCl	Sphalerite	ZnS
Hematite	$Fe_2O_3$	Staurolite	Fe <sub>2</sub> Al <sub>9</sub> Si <sub>4</sub> O <sub>22</sub> (OH) <sub>2</sub>
Illite	K(Al,Mg,Fe) <sub>2</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	Sylvtite	KCl
Jarosite	$KFe(SO_4)_2$	Thenardite	Na <sub>2</sub> SO <sub>4</sub>
Kaolinite	$Al_2Si_2O_7·2H_2O$	Tourmaline	(Na,Ca) (Fe,Mg,Al) <sub>3</sub> (Al,Fe) <sub>6</sub> (BO <sub>3</sub> ) <sub>3</sub> Si <sub>6</sub> O <sub>18</sub> (OH) <sub>4</sub>
Keramolite	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·16H <sub>2</sub> O	Zircon	Si <sub>6</sub> ZrSiO <sub>4</sub>

**Table 18.1** Mineral species found in coals. This is not a complete catalog of all minerals found in coals, nor do all of these minerals occur in the same coal.

Fewer than 20 are found in sufficient quantity to be important in the practical use of coals. These roughly 20 minerals can be grouped into six families. These families are discussed in the paragraphs that follow, along with examples of the kinds of reaction these minerals undergo during coal utilization.

Clays are usually the predominant minerals in coals. They can account for more than half of the total minerals content. Although the family of clay minerals is very extensive, those common in coal are illite,  $K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$ , kaolinite,  $Al_2Si_2O_5(OH)_4$ , and montmorillonite,  $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2$ . In general, clays are hydrous oxides of silicon and aluminum that contain other cations, such as the alkali and alkaline earth elements and iron, in the structure. Clays probably washed into the swamp during the accumulation and diagenesis of organic matter. They contribute aluminum and silicon to the ash, along with lesser amounts of other elements, such as potassium.

The principal carbonates are those of calcium, magnesium, or iron – calcite, magnesite, and siderite, respectively. Mixed carbonates also occur, particularly dolomite with calcium and magnesium, or ankerite, with iron, calcium, and magnesium. Carbonates precipitate by direct reaction:

$$Fe^{+2} + CO_3^{-2} \rightarrow FeCO_3$$
,

or by pH changes:

$$Ca^{+2} + 2 HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O_2$$

Calcite decomposes in the range 600–950°C:

$$CaCO_3 \rightarrow CaO + CO_2$$
.

Calcium oxide reacts readily with clays or with quartz. It is also capable of reacting with sulfur-containing gaseous species:

$$\begin{aligned} &\text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4, \\ &\text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O}. \end{aligned}$$

Calcium compounds, whether present initially in the coal or added in the form of limestone, can capture sulfur in combustion and gasification systems. Provided that the sulfate or sulfide is stable at the process temperatures, calcium-rich ashes or added limestone can function to reduce emissions of gaseous sulfur compounds.

Dolomite and ankerite decompose in about the same temperature range as the other carbonates. The magnesium, calcium, and iron liberated from decomposition of these minerals participate in aluminosilicate formation and act as fluxes. Magnesium and calcium from decomposition of dolomite can also react with silica to form diopside,  $CaMgSi_2O_6$ .

Siderite decomposes to wustite (FeO) and carbon dioxide in a slightly higher temperature range, generally about 400–800 °C. When siderite decomposition or pyrrhotite oxidation occurs, wustite oxidizes to magnetite,  $Fe_3O_4$ , or to hematite,  $Fe_2O_3$ . Which of these higher oxides is the stable product depends on temperature and oxygen partial pressure.

Silica, primarily in the form of quartz, can account for up to 20% of the total minerals in coals. Some silica can come from phytoliths, but most is probably washed into the swamp.

The major sulfide mineral is pyrite,  $FeS_2$  [D]. Most pyrite accumulates by precipitation after the coal has formed. Though sulfides usually amount to less than 5% of the total minerals in most coals, they receive much more attention than the concentration might at first seem to warrant. During combustion, sulfides produce sulfur oxides, which contribute to air pollution problems such as acid rain. Sulfur in coking coals can be incorporated in the coke. During smelting of a metal, sulfur gets into the metal, where it precipitates iron sulfides in the boundaries between individual grains. These iron sulfides weaken the metal in subsequent forming operations, such as hot rolling. "Spontaneous" combustion of coal stockpiles may be initiated by heat released from oxidation of pyrite in air. However, in coal liquefaction, pyrite could function as an *in situ* hydrogenation catalyst [E]. Some trace elements also occur in coals as sulfides, examples being lead, as galena, and zinc, in sphalerite.

	Si	Al	Fe	Ca	Mg	Na	K	S
Clays	√	√					√	
Carbonates			$\checkmark$	$\checkmark$	$\checkmark$			
Silica	$\checkmark$							
Sulfides			$\checkmark$					$\checkmark$
Salt						$\checkmark$		
Sulfates			$\checkmark$	$\checkmark$				√

Table 18.2 Contribution of inorganic elements to coals from the principal mineral families.

Pyrite decomposes to pyrrhotite at 300–600°C. The reaction can be written as

$$FeS_2 \rightarrow FeS + S.$$

Pyrrhotite is actually a non-stoichiometric compound in which the atomic S/Fe ratio is not exactly 1.00. What happens to the sulfur depends on the atmosphere in which the pyrite is decomposing. In a reducing atmosphere, sulfur forms hydrogen sulfide, so the net reaction is

$$FeS_2 + H_2 \rightarrow FeS + H_2S.$$

But, in an oxidizing atmosphere sulfur forms sulfur dioxide, as

$$FeS_2 + O_2 \rightarrow FeS + SO_2$$
.

Subsequent oxidation of pyrrhotite to iron(II) oxide results in the formation of lowmelting phases. FeO and FeS form a eutectic phase at 930°C. In oxidizing environments, FeO interacts with aluminosilicates to form various iron aluminosilicates.

Salt occurs in coals formed from organic matter that accumulated in marine environments. It occurs in some coals of the United Kingdom, central Europe, and Australia, but salt is rare in most coals of the United States. Salt exacerbates corrosion of metals. Chloride from the salt contributes to formation of hydrogen chloride during combustion. The hydrogen chloride dissolves in any available moisture to form corrosive hydrochloric acid.

Sulfates occur in low concentration, if at all, in most coals. Sulfates of iron and calcium are most common. Iron sulfate is likely to have arisen from the air oxidation of pyrite. Calcium sulfate is normally present as the dihydrate, gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O. Gypsum decomposes first to bassinite, CaSO<sub>4</sub>· $\frac{1}{2}$ H<sub>2</sub>O, and then to anhydrite, CaSO<sub>4</sub>. Anhydrite forms several eutectics that melt in the range 700–900°C, with sodium chloride, potassium sulfate, or sodium sulfate. At ≈900°C anhydrite decomposes to calcium oxide and sulfur oxides. In strongly reducing conditions, i.e. with abundant carbon monoxide, anhydride is reduced to calcium sulfate:

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2$$

Table 18.2 summarizes the principal inorganic elements contributed to coal – and ash – by the various minerals.

## 18.4 Coal cleaning

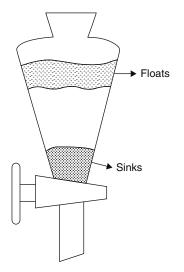
In almost all applications, the inorganic components of coals contribute nothing positive to utilization. Reducing the amount of inorganic components increases the calorific value on an as-received basis; when coal is transported, this means that more energy is being shipped per unit weight of fuel, or per unit shipping cost. During utilization, the ash has to be collected, handled, and disposed of in environmentally acceptable ways. The lower the inorganic content, the less effort (and expense) that needs to be devoted to ash handling. Pyrite adds to sulfur oxide emissions during combustion, so removing pyrite from coal can help in meeting emission regulations. In converting coal to metallurgical coke, inorganic components can dilute the important intermediate plastic phase (Chapter 23), interfering with coke formation, and when carried into the coke, can introduce undesirable impurities into the metal being produced.

The term *coal cleaning* refers to reduction of inorganic components, or loosely speaking, reduction of ash. Whether, and how extensively, a coal is cleaned before use depends on the market specifications, such as heating value, ash, and sulfur, that must be met to sell the coal competitively. As commonly practiced, coal cleaning relies on differences in physical properties between the carbonaceous portion of the coal itself and the inorganic constituents.

The success of a coal cleaning operation depends in part on how the mineral constituents are distributed through the carbonaceous part of the coal. Coals in which most of the minerals are epigenetic may have large mineral particles deposited in major cracks, or along the natural bedding planes. Simple crushing or grinding operations often suffice to liberate these mineral particles from the coal itself. In contrast, syngenetic minerals may occur in small particles, dispersed through, and intimately mixed with, the carbonaceous material. For coals like these, it may be impractical or prohibitively expensive to grind the coal fine enough to liberate the minerals for separation. Mineral grains, usually of small size, encased completely by the carbonaceous portion of the coal, are called inherent mineral matter, or included minerals. Often these are syngenetic. Those mineral particles not intimately mixed are referred to as excluded minerals, or extraneous mineral matter, and commonly represent epigenetic minerals.

Depending on rank and petrographic composition, the density of the carbonaceous portion of coal is 1.2-1.6 g/cm<sup>3</sup>. Quartz and the clay minerals have densities of  $\approx$ 2.6 g/cm<sup>3</sup>, and pyrite, about 5 g/cm<sup>3</sup>. In principle, treating coal in a medium having a density intermediate between that of the carbonaceous part of the coal and that of the inorganics should allow a sharp separation, with the coal itself floating and the minerals sinking. In practice, the separation is never perfect. For minerals easily liberated from the coal during grinding, density separation becomes straightforward. But, other minerals may have formed as tiny grains in coalified plant cell cavities (e.g. in fusinites) or may have become intimately mixed with the carbonaceous material by being washed into the swamp as the organic matter is accumulating. Generally it is not economically feasible to grind coal finely enough to liberate such extremely small mineral grains. No possible amount of grinding could liberate the cations bonded to the carboxyl groups in low-rank coals. Thus the extent to which crushing or grinding liberates minerals for subsequent removal depends on how they are held in the coal. There is no way to predict in advance - from the rank classification, for example how a given coal will respond to cleaning. Each coal has to be evaluated in the laboratory.

The success of any cleaning process, whether laboratory evaluation or commercial operation, depends on the size distribution of the coal used. As a rule, the smaller the particle size, the more minerals are liberated from the coal and the better the separation. However,



**Figure 18.1** A simple separation into low-density coal-rich particles, and high-density mineral-rich particles can be effected in the laboratory using a separatory funnel and a liquid medium of desired density.

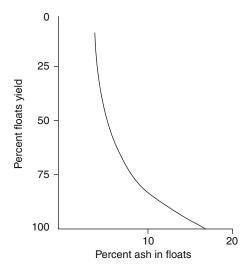
size reduction of the coal must be tempered by what is practical and economic, and by the particle size requirements of the equipment in which the coal eventually will be utilized.

The float-sink test provides an approach to assessing the cleaning of a given coal sample. This test involves shaking a sample of pulverized coal with liquid of known density, either an aqueous solution of a salt such as calcium chloride, or an organic liquid. A density separation should occur, as shown in Figure 18.1.

The carbon-rich material is called the floats; the mixture of minerals and inorganicrich coal makes up the sinks. Plotting the yield of floats as a function of the ash value of the floats (determined from proximate analysis) provides a useful preliminary evaluation. Figure 18.2 shows an example.

The data points in such a curve would have been obtained by using a series of liquids of increasing density. A 100% floats yield is equivalent to recovering the entire original sample of coal in the floats. Thus the intersection of the curve with the abscissa represents the ash value of the original coal. For many coals, the curve asymptotically approaches the ordinate. This means that density separation cannot clean the coal completely, i.e. to a 0% ash value. The ash value of the floats at which the curve becomes essentially vertical, sometimes called the residual ash, results from those mineral particles that were too small to be liberated by grinding and the inorganic components chemically bonded to the coal. Such a float-sink curve provides an estimate of the "penalty" involved in cleaning coal. In the example of Figure 18.2, a reduction of ash value from 10% to 5% would correspond to a floats yield decreasing from about 78% to about 42%; the floats yield would have decreased by about half.

Separation in a float-sink test is not always as sharp as indicated in the sketch of Figure 18.1. Sometimes material remains in suspension in the liquid, being known as middlings. The middlings represent a potential problem, in that they do not appear with the floats and, in an actual cleaning operation, might be difficult to separate from the cleaning liquid.



**Figure 18.2** An example of the variation of floats yield as a function of the ash value in the floats. The inverse relationship means that there is a trade-off between how clean (i.e. low ash value) the floats are and the amount that can be recovered.

A washability curve, see Figure 18.3, provides a more detailed appraisal of coal cleaning. These curves can be used in several ways. One is to determine the cleaning performance of a liquid of a given density, say,  $1.5 \text{ g/cm}^3$ . In this case, one would read from the density axis at point 1.5 to curve **2**. Finding the value of this intersection on the floats yield axis gives a predicted floats yield of 80%. Reading from 80% on the floats yield axis to curve **1** and finding the value of this intersection on the ash axis shows that there would be an ash yield of 7.5% from the floats. And, reading from the 1.5 g/cm<sup>3</sup> value on the density axis to curve **3** shows a middlings yield of 9%.

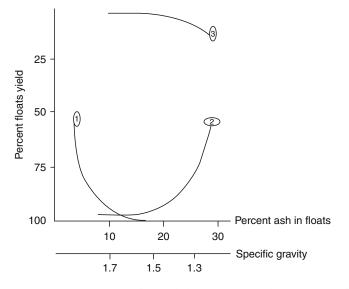
Washability curves can also be used to determine the density necessary to attain a desired ash value in the cleaned coal, i.e. evaluating the performance of the cleaning process. Suppose, as an example, the target is a coal of 6% ash value. By reading from 6% on the ash axis to curve 1 and finding the value of the intersection on the floats yield axis shows that the floats yield for a 6% ash cleaned coal would be 75%. Reading from 75% on the floats yield axis to curve 2 and finding the density equivalent to the intersection point indicates a yield density of 1.4 g/cm<sup>3</sup>. Reading from this point on the density axis to curve 3 gives a middlings yield of 13%.

The distribution coefficient, c, expresses the performance of separation at a particular density. It is found from

$$c_x = 100 \, F/(F + S),$$

where the subscript x specifies the density for which c is being determined; F, the weight percent coal in the floats; and S, the weight percent in the sinks. The point at which the distribution coefficient is 50% is called the Tromp cut point.

Heavy media separation involves adding coal to a vessel with a suspension of some mineral – most commonly, magnetite,  $Fe_3O_4$  – that provides a density intermediate between the coal and minerals. Coal particles rise to the surface and are collected from the top of the vessel. The mineral-rich coal and separated minerals, referred to as



**Figure 18.3** An example of a washability curve. Such a curve could be used to determine the cleaning performance of a liquid of given density, or to determine the density of a liquid needed to obtain a desired ash value in the floats.

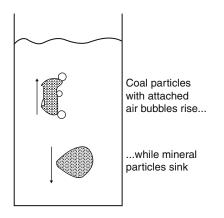
discards, are withdrawn from the bottom. Magnetite is favored for two reasons. First, it has a high density,  $5.2 \text{ g/cm}^3$ , so not much magnetite is needed to produce a slurry having a density of, say,  $1.5 \text{ g/cm}^3$ . Second, magnetite is magnetic, so it can be separated and recovered for re-use using magnetic separators.

Froth flotation takes advantage of differences in surface properties between coal and minerals, as well as differences of density. A sample of finely pulverized coal consists of particles that are coal-rich and others that are mineral-rich. The surface of bituminous coals and anthracites is composed of hydrophobic hydrocarbon macromolecules. In contrast, many common minerals, such as clays and quartz, have hydrophilic surfaces. High concentrations of oxygen atoms on the surfaces of these mineral particles provide numerous sites for hydrogen bonding of water molecules. The flotation process involves blowing air through a mixture of finely crushed coal in water. Dense, hydrophilic mineral particles are wetted by the water and sink. Hydrophobic coal particles are not wetted, but rather air bubbles can attach to the surface of the coal particles and carry them to the liquid surface (Figure 18.4).

A sketch of a flotation cell is shown in Figure 18.5 to illustrate the operation; Figure 18.6 provides a more detailed diagram of a commercial unit.

Separation of coals from minerals is never complete, because not all minerals are liberated by grinding, some minerals may be hydrophobic and thus attach to air bubbles and float, and some coal particles may be hydrophilic, especially if they have oxygen functional groups on their surface.

Chemical cleaning of coal has been the subject of much research in recent decades, mainly with a focus on reducing sulfur content. Many approaches have been explored in the laboratory, with some promising results at that scale. None has been adopted for commercial use. This is due in part to process economics, because it is difficult to



**Figure 18.4** This sketch illustrates the process of flotation, which takes advantage of the differences in "wettability" between hydrophilic and hydrophobic surfaces.

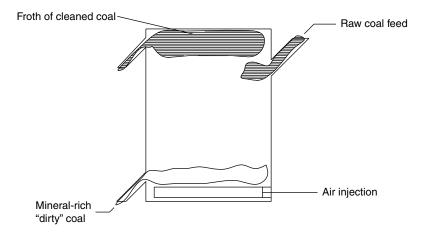
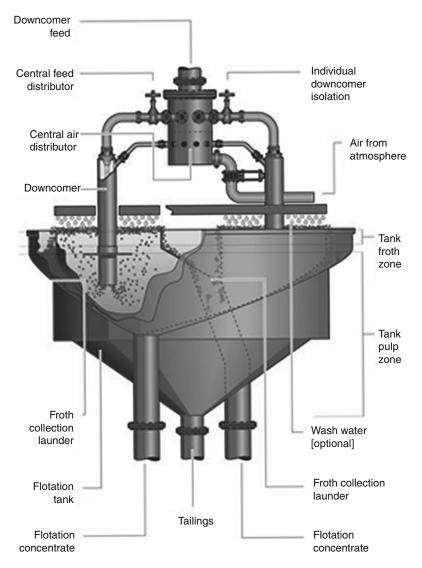


Figure 18.5 Operation of a flotation cell.

find a chemical process that is cheaper to use than a relatively simple physical separation. Some attention has been directed to use of bacteria or fungi to metabolize sulfur-containing compounds in the coal. There, part of the problem has been in kinetics, the biochemical reactions being so slow that immense quantities of coal would have to be "in process" to achieve output rates needed for operation of, e.g., power plant boilers.

## 18.5 Behavior of inorganic components during coal utilization

Because most of the world's coal is utilized in high-temperature processes – combustion and gasification – knowledge of the behavior of ash at high temperatures is important for design and operation of coal utilization equipment. A useful assessment comes from measuring the ash fusion temperatures (AFTs). An ash sample is shaped into a triangular pyramid, then heated under controlled conditions. Usually four transition temperatures are noted: the initial deformation temperature, at which the pointed apex



**Figure 18.6** A commercial Jameson flotation cell from Xstrata Technology. In this type of cell the air is injected through a downcomer in the top of the cell, different from air injection in the bottom, as shown in Figure 18.5.

of the pyramid begins to become rounded; the softening temperature, at which melting has proceeded to a point at which the height of the remaining pyramid is equal to the width of its base; the hemispherical temperature, at which the height is half the width of the base; and the fluid temperature, at which the sample has melted to the extent of spreading over its entire ceramic support. Values of AFTs depend on whether the measurement was made in an oxidizing or reducing atmosphere. In the latter, iron compounds become reduced to the Fe(II) oxidation state and act as fluxes, whereas Fe(III) compounds, existing in an oxidizing atmosphere, do not.

As the temperature of the coal is raised in the early stages of combustion, a complex sequence of phase changes and reactions occurs. At some point, the temperature can

Temperature, degrees C	Reactions or phase transformations
300	$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot \frac{1}{2}H_2O$
400	$\begin{array}{l} K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_4 \cdot nH_2O \rightarrow K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_4\\ CaSO_4 \cdot {}^{1\!\!/}_2H_2O \rightarrow CaSO_4 \end{array}$
450	$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7$
600	$\begin{array}{l} \alpha\text{-SiO}_2 \rightarrow \beta\text{-SiO}_2 \\ FeS_2 \rightarrow FeS \end{array}$
700	$K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_4 \rightarrow K(Al,Mg,Fe)_2(Si,Al)_4O_{10}$
750	CaSO <sub>4</sub> -NaCl eutectic melts
	$Clays + CaCO_3 + FeS_2 \rightarrow melt phase$
	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O \rightarrow (Na,Ca)_{0.33}(Al, Mg)_2Si_4O_{10}(OH)_2$
800	$FeCO_3 \rightarrow FeO + CO_2$
	$Ca(Mg,Fe)(CO_3)_2 \rightarrow CaO + MgO + FeO + CO_2$
900	$K_2SO_4$ -CaSO <sub>4</sub> eutectic melts
	$PbS \rightarrow PbO$
	$\beta$ -SiO <sub>2</sub> $\rightarrow$ tridymite
	$CaMg(CO_3)_2 \rightarrow CaO + MgO + CO_2$
	$3 \text{ CaSO}_4 + \text{CaS} \rightarrow 4 \text{ CaO} + 4 \text{ SO}_2$
950	$2 \text{ Al}_2\text{Si}_2\text{O}_7 \rightarrow 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{SiO}_2$
	FeO–FeS eutectic melts
	$CaCO_3 \rightarrow CaO + CO_2$
	$2 \text{ CaO} + \text{Al}_2 \text{Si}_2 \text{O}_7 \rightarrow \text{Ca}_2 \text{Al}_2 \text{SiO}_7 + \text{SiO}_2$
	$CaO + Al_2Si_2O_7 \rightarrow CaAl_2Si_2O_8$
1000	$TiO_2$ (anatase) $\rightarrow$ $TiO_2$ (rutile)
1100	K(Al,Mg,Fe) <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> forms glassy phase
1200	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> forms glassy phase
1300	Glassy phases transform to spinels and Si-rich glass
1400	$Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ melt
	FeO melts
	Glassy phases $\rightarrow 2Al_2O_3$ ·SiO <sub>2</sub>
1500	$SiO_2$ (tridymite) $\rightarrow SiO_2$ (cristobalite)

**Table 18.3** A summary of some of the principal mineral transformations under oxidizing conditions, and the approximate temperature at which they occur.

become high enough to allow those inorganic components with relatively low melting points to soften, or melt outright. Often, these components are aluminosilicates, formed by thermal alteration of clay minerals, and, in low-rank coals, from reactions of clay minerals with cations liberated from the decomposition of carboxylate salts.

Table 18.3 summarizes some of the transformations of mineral matter in coals with increasing temperature, in oxidizing atmosphere. The temperatures reported are approximate values; transformations observed in practical operating equipment do not necessarily agree with exact values from phase diagrams or other slow-heating, equilibrium situations, because of differences in heating rates and residence times at temperature.

Table 18.3 by no means represents a complete catalog of all phase transitions and reactions occurring among the inorganic components of coals. It is intended to be

illustrative of the kinds of process that occur, and to convey a sense of the extraordinary complexity of coal ash chemistry.

Some mineral particles, particularly those of excluded minerals, undergo fragmentation during heating. Several effects contribute to particle fragmentation. These include thermal shock caused by very rapid heat-up, build-up of internal pressure caused by gases evolved from thermal decomposition reactions, or even mechanical attrition when mineral particles collide at high velocities.

While AFTs have been a useful and widely accepted approach for characterizing the high-temperature behavior of ash, some chemical and physical transformations, including partial melting, agglomeration, and sintering, can occur at temperatures below even the initial deformation temperature. Cations associated with carboxylate groups in low-rank coals become mobile when the carboxylate groups are lost during thermal decomposition of the coal. At about the same time, clay minerals lose water of hydration and undergo structural transformations or solid-state phase changes. The liberated cations interact with the clays as they rearrange, to form low-melting alkali or alkaline earth aluminosilicates. Kaolinite reacts with pyrite and calcite to form melt phases around 750°C. Quartz is not so reactive as clays, but nevertheless reacts with alkalis or iron compounds to form low-melting phases.

Inorganic components, when considered as oxides, fall into two categories: acidic oxides act as oxide ion acceptors, forming anions such as silicates and aluminates; basic oxides are oxide ion donors. The acidic oxides form large oligomeric or polymeric network structures based on shared oxide ions. These materials tend to have high melting points, and high viscosities in the melt phase. The oxides of silicon, aluminum, and titanium act as acidic oxides. By donating oxide ions, basic oxides disrupt the metal–oxygen–metal networks, creating smaller-sized structures having lower melting points and lower viscosities when they melt. The alkali and alkaline earth elements function as basic oxides; that is, they act as fluxes. Of the major metallic elements in coals, only iron can exist in different stable oxidation states. In oxidizing atmospheres, iron(III) is stable, whereas iron(II) dominates in reducing atmospheres. Iron(III) usually acts as an acidic oxide, counting among the network-forming components. Iron(II) behaves like a basic oxide, resulting in lower melting points and viscosities. Unless ashes have very low concentrations of iron, their behavior, such as AFTs, is different in oxidizing atmospheres.

Many empirical correlations of AFTs with composition have been developed. Most involve calculating one or more parameters of composition that take into account the effects of acidic oxides in contributing to high AFTs, and basic oxides in lowering these temperatures. The methods differ in detail, and often resort to graphical methods of estimation once some parameter(s) of composition have been calculated. All, however, recognize the role of sodium and potassium in reducing AFTs, and the effect of iron in reducing atmospheres.

The terms sintering and agglomeration are sometimes used interchangeably, but do not quite refer to the same thing. Agglomeration results in formation of large clusters of ash particles. Two features characterize the agglomeration process. First, the partially or completely molten phase that acts to stick the agglomerates together – i.e. the "glue" – does not necessarily arise from the agglomerated particles themselves. That is, ash particles could become coated with a sticky layer as a result of, e.g. vapor-phase deposition of a low-melting phase, or from contact with a molten phase produced by melting of

other ash constituents. Second, though the agglomerate itself grows in size, little or no change occurs in size of the individual ash particles incorporated into the agglomerate. In comparison, in sintering, bonding between particles comes from a melt phase that results from partial melting of the particles undergoing sintering. The original ash particles coalesce into larger particles, just as in the sintering of catalyst particles on a support (Chapter 13). In fixed-bed combustors, such as stoker-fired units, sintering of the ash results in the formation of clinkers, hard aggregates of ash particles that could be troublesome for operation of ash collection and handling equipment. In fluidized-bed units, sintering of the ash, or ash plus bed material, can form aggregates too large to be fluidized by the air stream passing through the bed. This can also lead to serious operational problems, including "de-fluidizing" the bed.

In pulverized-coal-fired combustors a portion of the ash particles becomes entrained in the rapidly flowing stream of combustion gases. These particles can impact, and adhere to, heat-transfer surfaces in the boiler. The resulting deposit, sometimes referred to as ash fouling, reduces heat transfer to the water or steam. To maintain the desired steam temperature, it becomes necessary to increase the firing rate, which in turn increases the temperature inside the combustor. The increased temperature exacerbates ash fouling, because increasing the temperature in the interior of the combustor provides a greater chance for sintering of the ash deposit. Further, a partially molten surface of ash provides an efficient trap for collecting and retaining other ash particles as they continue to impact the surface. The ash deposit will continue to grow, setting off a cycle of increasing firing rates and growth of deposit. If the deposits cannot be removed easily [F], the combustor has to be shut down periodically for cleaning. In extreme cases, the ash deposits can grow so large that eventually they break away from the boiler surfaces, and cause serious damage to the boiler as they hurtle down through the unit.

The extreme case is slagging, formation of a free-flowing liquid stream of molten ash. Some coal combustion systems have been designed to operate in the so-called slagging mode, in which the ash is deliberately melted so that it can be collected as it flows out of the combustor. In that case, temperatures in the combustor have to be kept high enough to insure that the flowing slag has a sufficiently low viscosity to flow to, and out of, the unit into the slag handling system. On the other hand, pulverizedcoal-fired combustors, the dominant technology in the use of coal for electricity generation, are not usually designed to cope with running slag. In such units, slagging is a serious problem that can damage the boiler or require unscheduled outages for cleaning and maintenance. Similarly, gasifiers are designed to operate either with slagging, or not. (Units in which the ash does not melt, but rather accumulates and is removed as a solid, are sometimes called dry-ash or dry-bottom gasifiers or combustors.) Matching the fusion characteristics of the ash with the designed operating mode of the equipment in which the coal will be used is absolutely vital for successful operation.

A rule of thumb suggests that ashes with softening temperatures <1200°C represent slagging coals, while those with softening temperatures >1425°C are non-slagging. Those ashes that fall into the gap in the middle could be slagged or not, depending on operating temperatures and heat-release rates in the unit. In some cases, the operators might have leeway to adjust these two parameters to keep running in the face of variation in the AFTs of the feed coal.

For combustors or gasifiers designed to operate in a slagging mode, viscosity characteristics of the slag, particularly the temperature dependence of viscosity, have an important role in maintaining reliable operation. When all ash components are in the melt phase, slags act as Newtonian liquids. Slag viscosity increases gradually as its temperature drops. Continued cooling of the slag eventually reaches a point at which one or more components crystallize from the melt, producing a two-phase mixture. This behavior takes place at the temperature of critical viscosity,  $T_{cv}$ . Below  $T_{cv}$  the slag becomes non-Newtonian. Its viscosity increases rapidly with further decrease in temperature; the slag is headed toward solidification. A slagging combustor or gasifier is now in serious trouble, requiring prompt and effective intervention if a shut-down is to be avoided.

Viscosity of slag decreases as the base-to-acid ratio increases, for comparisons made at identical temperatures. The base-to-acid ratio is found from

$$Base/Acid = (Fe_2O_3 + CaO + MgO + Na_2O + K_2O)/(SiO_2 + Al_2O_3 + TiO_2),$$

where the molecular formulas represent the weight percent of these constituents in the slag, on an SO<sub>3</sub>-free basis. In this equation, iron is assumed to act as a base, and is included with other basic oxides, even though it appears in the analysis report as  $Fe_2O_3$ .

Numerous approaches have been developed to calculate slag viscosity from composition. No predictive equations based on first principles exist; however, many empirical correlations have been developed to predict slag viscosity and its changes with temperature from the ash composition. Usually the intent is to perform the calculation for a series of temperatures, to obtain a viscosity–temperature curve for the slag of interest. The Watt–Fereday model provides a useful example. In this model, composition is first normalized so that

$$SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO = 100\%$$
.

Then two terms, M and C, are calculated from these normalized compositions:

$$M = 0.00835 \operatorname{SiO}_2 + 0.00601 \operatorname{Al}_2 \operatorname{O}_3 - 0.109 - 3.92.$$

$$C = 0.0415 \operatorname{SiO}_2 + 0.0192 \operatorname{Al}_2 \operatorname{O}_3 + 0.0276 \operatorname{Fe}_2 \operatorname{O}_3 + 0.0160 \operatorname{CaO} - 4.92$$

Finally, viscosity is determined from

$$\log \eta = [10^7 M / (T - 150)^2] + C,$$

where  $\eta$  is the viscosity in poises (1 poise is 0.1 pascal-seconds). The Watt–Fereday equation was developed for British bituminous coal ash slags, but gives reasonably satisfactory results for other coals having slag compositions of 29–56% SiO<sub>2</sub>, 15–31% Al<sub>2</sub>O<sub>3</sub>, 2–28% Fe<sub>2</sub>O<sub>3</sub>, 2–27% CaO, and 1–8% MgO. Models for calculating AFTs or viscosities can fail badly when applied to ashes or slags having compositions outside the range for which the model was initially developed.

Two additional ash-related problems can arise: erosion and corrosion. Impact of relatively hard mineral particles against surfaces inside combustors or gasifiers causes erosion. The problem is complex, the degree of erosion depending on numerous factors that include the hardness of the ash particles, their size and shape, and the velocity and angle with which they impact the surface. Quartz can be a particular problem, in effect sand-blasting the surfaces it contacts.

Sulfur oxides have a major role in corrosion, via their conversion to sulfuric acid:

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3,$$
  
 $SO_3 + H_2O \rightarrow H_2SO_4$ 

Salt, other chloride minerals, or organically bound chlorine can convert to hydrogen chloride, which is quite soluble in water. If combustion gases cool below the dew point, the interior of the boiler can be treated to a rain of hydrochloric acid. Many alloys, including stainless steels, resist corrosion by forming a tightly bonded layer of oxides on the metal surface. The oxide layer serves to protect the metal underneath. Depending on their composition, ash deposits on such surfaces could interact with the protective oxide layer on the metal, compromising its ability to protect it, and thereby hastening corrosion.

## Notes

- [A] An example of an organometallic compound that was once important in fuel chemistry is tetraethyllead,  $(C_2H_5)_4Pb$ . This compound was used during the previous century as an octane-booster in gasoline, the product marketed as "leaded" or "ethyl" gasoline. Its use was discontinued because lead poisons the catalyst in the catalytic converters used to reduce exhaust emissions.
- [B] Numerous variations exist for the chemical fractionation method. In some laboratories, the coal is first leached with distilled or deionized water, to remove water-soluble salts. Sometimes the ammonium acetate leaching step is followed by treatment with ethylenediamine tetra-acetic acid (EDTA), to extract metals from coordination sites. A hydrofluoric acid treatment can be omitted, with all species insoluble in dilute hydrochloric acid considered to be silicates and pyrite. Other acids, such as nitric, can be used. Nonetheless, the basic concept involves use of a series of reagents of increasing extracting or solvating power, to discriminate between several modes of occurrence for the elements.
- [C] In the Cold War and Red Scare atmosphere of the 1950s, there was intense interest in finding domestic sources of uranium in the United States, primarily for nuclear weapons. Some lignites have enough uranium to have been considered, in those days, as uranium ores rather than as a fuel. From time to time there has been interest in recovering elements valuable in solid-state electronics, such as gallium and germanium, from ash.
- [D] There are two minerals of formula FeS<sub>2</sub>, pyrite and marcasite, with different crystal structures. Usually no attempt is made to differentiate between them, and both are lumped together as "pyrite."
- [E] The catalytically active species is likely to be the reduction product of pyrite, the non-stoichiometric sulfide  $FeS_x$ , known as pyrrhotite. Probably the non-stoichiometric solid has surface defects that provide catalytically active sites, much as a cobalt-promoted  $MoS_2$  catalyst for hydrodesulfurization.
- [F] Ash deposits that are not tightly bonded to the underlying metal surface, and are not strongly sintered or agglomerated, can be removed with a jet of high-pressure water or steam. If the ash deposits are mechanically strong due to sintering, and tightly adhere to the internal surfaces in the boiler, the problem becomes a whole lot

thornier. Some power stations have resorted to using shotguns to weaken or loosen the deposits enough so that they will fall off or be susceptible to sootblowing. And, extreme cases require extreme remedies. One such is use of the nitrate ester of glycerol, absorbed in a material like kieselguhr (Chapter 13). The common name for this product is dynamite.

#### Recommended reading

- Berkowitz, Norbert. *An Introduction to Coal Technology*. Academic Press: New York, 1979. This book remains a superb introduction to the field. Chapters 2 and 10 have information pertinent to the present chapter.
- Durie, Robert A. *The Science of Victorian Brown Coal*. Butterworth-Heinemann: Oxford, 1991. An edited collection of chapters that provides a comprehensive survey of this important coal resource. Chapters 5 and 11 provide much useful information on the inorganic chemistry of Australian brown coals and the behavior of these components in utilization.
- England, T., Hand, P.E., Michael, D.C., Falcon, L.M., and Yell, A.D. *Coal Preparation in South Africa*. South African Coal Processing Society: Pietermaritzburg, 2002.
  A comprehensive review of coal preparation, with primary focus on South African practice. Chapters 6 through 9 are especially relevant to the present chapter.
- Konar, B.B., Banerjee, S.B., Chaudhuri, S.G., et al. Coal Preparation. Allied Publishers: New Delhi, 1997. Chapter 4 of this monograph is particularly relevant to the present chapter, discussing coal washing with primary emphasis on the coals of India.
- Leonard, Joseph W. *Coal Preparation*. Society for Mining, Metallurgy, and Exploration: Littleton, CO, 1991. An edited collection of chapters on all aspects of coal preparation, including coal cleaning. Very thorough and comprehensive, and an excellent resource for those interested in, or working in, this field.
- Raask, Erich. *Mineral Impurities in Coal Combustion*. Hemisphere: Washington, 1985. A very thorough monograph on ash behavior in combustion, probably still the best one available.
- Schobert, Harold H. *Lignites of North America*. Elsevier: Amsterdam, 1995. While not intended as a companion volume to the book by Durie (above), together these two books survey all aspects of two of the world's major sources of low-rank coals. Chapters 5, 6, and 11 are particularly related to the present chapter.

A mixture of carbon monoxide and hydrogen is called synthesis gas, because it can be used to synthesize a variety of useful and valuable products, as explained in Chapter 21. Synthesis gas can be made from virtually any carbon-containing material, including all of the fossil and bio- fuels discussed in this book, and others that are not (such as municipal or agricultural wastes or used tires). Generically, the reaction is

"C" + 
$$H_2O \rightarrow CO + H_2$$
,

where "C" is used simply to represent a carbon-containing feedstock, not implying it to be pure carbon. The reaction conditions and reactor design, and even different names for the process, are specific to individual feedstocks. Several terms are used, depending on the nature of the feedstock, to describe what is chemically the same process. Conversion of gaseous or light liquid hydrocarbons is called steam reforming. Partial oxidation uses heavy oils from petroleum or oil sands. And, if solid biomass or coal is the feed, the process is called gasification. Regardless of names, the reaction of carbon-containing feedstocks with steam provides immense versatility to produce, and later employ, synthesis gas.

An important aspect of synthesis gas production is the versatility of what can be done with the product: synthesis gas can be used directly as a gaseous fuel; converted to methane (substitute natural gas); converted to methanol, to be used directly as a liquid fuel or converted further to gasoline; or converted to a variety of other liquid hydrocarbon fuels. When using coal as the feedstock, some of the impurities in the coal – notably sulfur and mineral matter – can be removed at the same time. Further, it is easier to capture  $CO_2$  from concentrated gas streams associated with synthesis gas processes than from the relatively dilute flue gas streams produced in coal combustion.

## **19.1** Steam reforming of natural gas

Steam reforming of natural gas is the major route to synthesis gas today. Much of the synthesis gas is used to make methanol. It is also one of the major processes for making hydrogen, accounting for 90% of worldwide hydrogen production. Hydrogen is used as rocket fuel and in ammonia synthesis. Assuming natural gas to be pure methane, the reaction is

$$CH_4 + H_2O \rightarrow CO + 3H_2.$$

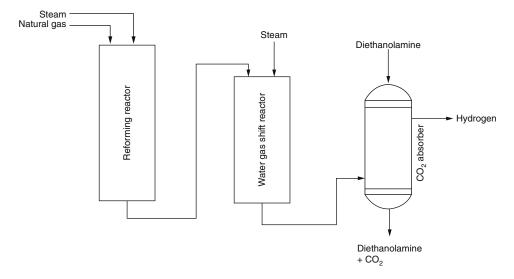


Figure 19.1 Process flow for steam reforming of natural gas.

Depending on the source of the gas and the extent to which it has been processed before steam reforming, there may be small amounts of ethane, propane, or butane. All react in analogous ways, i.e.

$$C_2H_6 + 2 H_2O \rightarrow 2 \quad CO + 5 H_2,$$
  
 $C_3H_8 + 3 H_2O \rightarrow 3 \quad CO + 7 H_2,$   
 $C_4H_{10} + 4 H_2O \rightarrow 4 \quad CO + 9 H_2.$ 

The reactions are not confined to alkanes. The reaction of steam with any hydrocarbon source can be described by the general equation

$$C_xH_y+x\ H_2O\to x\ CO+(x+\frac{y}{2})\ H_2.$$

Steam reforming is endothermic. Natural gas steam reforming uses externally fired furnaces, the heat coming from burning a portion of the gas. Typical conditions involve reaction at 850–900 °C and 3 MPa, in the presence of a nickel oxide catalyst supported on silica or alumina, with magnesium oxide (magnesia) promoter. Sulfur compounds in the gas poison these catalysts, so it is critical that the gas be sweetened upstream of steam reforming. (Sweetening is described in Chapter 10.) Sweetened gas can still be passed through a guard bed of zinc or iron oxide to absorb the last traces of sulfur:

$$FeO + H_2S \rightarrow FeS + H_2O.$$

Figure 19.1 provides a flow diagram for a steam reforming operation.

Unconverted methane is recycled. LPG or light naphtha also serve as good feeds to steam reforming. Two problems can be encountered. First, the high reaction temperature causes sintering of the nickel. As the particles of nickel grow, their surface area decreases, causing the activity of the catalyst to drop. The magnesium oxide promoter acts to retard sintering, probably by concentrating at the surface of the nickel particles and not being so susceptible to melting (compare the relative melting points of 2800 °C for MgO vs. 1453 °C for Ni). Second, a potential side reaction of hydrogen and carbon monoxide,

$$CO + H_2 \rightarrow H_2O + C$$
,

deposits carbon on the catalyst, analogous to coking discussed in Chapter 13.

An alternative route involves partial combustion of methane in the presence of supported nickel catalysts at 850–900 °C, though the reaction proceeds rapidly at 210–240 °C in the presence of copper/zinc supported catalysts. Reaction pressure is  $\approx$ 4 MPa. By-product carbon dioxide is removed by scrubbing with monoethanolamine. The net reaction is

$$2 \text{ CH}_4 + \text{O}_2 \rightarrow 4 \text{ H}_2 + 2 \text{ CO}.$$

If the intent is to couple this process with subsequent ammonia production, it can be run with a mixture of air and oxygen, so that the  $N_2/H_2$  ratio in the product gas has the desired value (0.33) for ammonia synthesis.

## 19.2 Partial oxidation of heavy oils

Conversion of heavy oils, distillation residua, asphalts, and oil from oil sands can be effected by the same basic process as steam reforming, though in this case called partial oxidation. The same generic equation for the reaction of steam with hydrocarbons applies. The steam–hydrocarbon reaction is endothermic, but exothermic reaction of a portion of the feed simultaneously, inside the reactor, provides the necessary heat to drive the steam–hydrocarbon reactions. The generic reaction is

$$C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O.$$

The process is a bit more complicated than externally heated steam reforming because of two factors: first, an equilibrium exists between the four gaseous products of these two reactions,

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$

This is called the shift reaction, or the water-gas shift. Water gas shift occurs during partial oxidation (and gasification, discussed later). However, its major importance comes from our being able to carry it out deliberately in a separate reactor, to adjust the relative proportions of carbon monoxide and hydrogen in the synthesis gas, discussed further in Chapter 20. Second, at the very high temperatures in a partial oxidation reactor ( $\approx$ 1300 °C), some of the feed can pyrolyze to solid carbon. Carbon is consumed in two reactions, steam gasification:

$$C + H_2O \rightarrow CO + H_2$$
,

and reaction with carbon dioxide:

$$C + CO_2 \rightarrow 2 CO.$$

The latter process is the Boudouard reaction [A].

The net process from these reactions is

$$C_xH_y + \frac{x}{2}O_2 \rightarrow x \operatorname{CO} + \frac{y}{2}H_2.$$

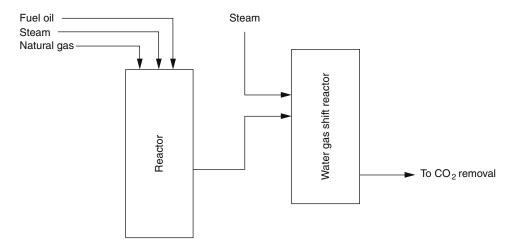


Figure 19.2 Process flow for partial oxidation of heavy oils, originally developed by Texaco.

The presence of oxygen on the left side of the equation justifies the name partial oxidation for this process.

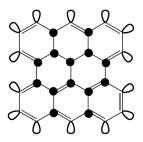
Industrially, partial oxidation is done to generate synthesis gas for subsequent conversion to ammonia, methanol, or light hydrocarbon liquids. Various companies have developed their own versions of partial oxidation. One such is the Texaco partial oxidation process (the Texaco partial oxidation and gasification processes were acquired by General Electric in 2003). It runs in a cylindrical steel pressure vessel that has provisions for feeding the heavy oil, steam, oxygen, and quench water, see Figure 19.2.

The reactions take place at 1100–1500 °C. The product gas is quenched with water in the bottom of the reactor. The product is about 97% carbon monoxide and hydrogen. The Texaco process can be used to treat a wide variety of feedstocks in essentially the same piece of equipment. Only the oil injection system needs to be changed, to accommodate the properties of the specific feed being used.

## 19.3 Coal and biomass gasification

The technology of converting coal to a gaseous fuel of any sort is called coal gasification. This section focuses mainly on gasification for production of synthesis gas. Gasification to make gaseous fuels for industrial or domestic heating and lighting was an important chapter in the history of fuel technology, but in most parts of the world is now obsolete. Much of the discussion about coal gasification can also be applied to biomass and various solid wastes or residues.

Why gasify coal? Coal is the cheapest natural hydrocarbon. It occurs in great abundance in many industrialized and developing nations, including China, India, Russia, the United States, South Africa, and Australia. Conversion of coal also provides opportunities for removing potential pollutants, e.g. ash and sulfur, at the same time. Gasification provides routes to clean gaseous and liquid fuels, augmenting the supplies of these fuels. Furthermore, gaseous or liquid fuels can be easier to ship and handle than solids. Coal-based integrated gasification combined cycle (IGCC) plants for electricity generation offer higher



**Figure 19.3** This structure of phenanthroperylene illustrates the difference between basal-plane atoms, indicated by black dots, and edge atoms, with an "unfulfilled valency" in  $\sigma$ -bonding orbitals. As a rule, edge atoms are more reactive.

overall efficiencies than conventional pulverized-coal-fired plants. In an IGCC plant, coal is gasified to produce clean fuel gas used to fire a combustion turbine. This turbine turns a generator for producing electricity. Hot exhaust gases from this turbine are used to raise steam, which is then passed into a steam turbine coupled to a second generator. With higher efficiency, more electricity can be produced from a given amount of coal consumed, or less coal (with fewer carbon dioxide emissions) can produce a given quantity of electricity.

## 19.3.1 Fundamentals of the carbon–steam and related reactions

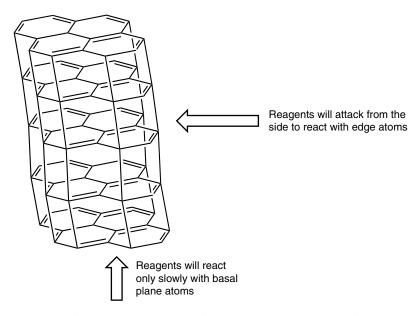
Consideration of the fundamentals of gasification can be simplified by assuming that coal is carbon. Of course it isn't, but the additional complexities brought in by the other elements can be added later, after considering the reactions of carbon. Various reactions occur during gasification, usually represented as the reactions of carbon with small gaseous molecules, e.g.

Combustion:	$C + O_2 \rightleftharpoons CO_2,$	(-395 MJ)
Boudouard reaction:	$C + CO_2 \rightleftharpoons 2 CO,$	(168 MJ)
Carbon-steam reaction:	$C + H_2 O \rightleftharpoons CO + H_2,$	(136 MJ)
Water gas shift reaction:	$CO + H_2O \rightleftharpoons CO_2 + H_2,$	(-32 MJ)
Hydrogenation:	$C + 2 H_2 \rightleftharpoons CH_4.$	(-92 MJ)

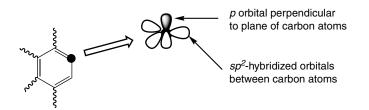
The enthalpy changes represent the reaction proceeding from left to right as written, and have units of MJ per kilogram-mole of carbon. The apparent simplicity of these equations is deceptive. The reactions can be complicated, in part because all are heterogeneous gas-solid reactions, and in part because all are equilibria, with the composition at equilibrium depending on temperature and pressure.

Different carbons display different reactivities toward these reagents. A pattern of selective reaction occurs, in which some sites on the carbon gasify readily, whereas other sites remain unreacted. Particularly reactive sites are called active sites. Active sites are located at the edges of carbon layers. As a rule, edge-site atoms show much higher reactivity than basal-plane atoms, see Figure 19.3.

In a three-dimensional structure, such as a graphite lattice (Figure 19.4) gaseous reactants attack the prismatic edge of the structure, rather than the basal planes. The rates of attack at the edge are two to three orders of magnitude higher than at the basal



**Figure 19.4** The greater reactivity of edge atoms in a crystalline stack of aromatic rings favors reaction on the sides rather than on the basal planes.



**Figure 19.5** All carbon atoms in an aromatic structure, including the edge atom shown as a black dot, have three  $sp^2$ -hybridized orbitals providing the  $\sigma$ -bonding between carbon atoms, and one *p* orbital perpendicular to the ring, which participates in the  $\pi$ -bonding network.

plane. The difference in reactivity derives partly from a difference in bonding. Let us consider an edge atom, as shown in Figure 19.5.

The  $sp^2$ -hybridized orbitals lie in the plane of the aromatic rings, while the nonhybridized *p* orbital is perpendicular to the plane. The non-hybridized orbital participates in the delocalized  $\pi$ -bonding system. Two of the three  $sp^2$  orbitals participate in  $\sigma$  bonding to adjacent carbon atoms, see Figure 19.6.

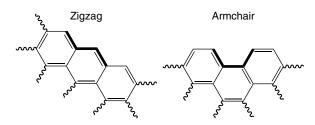
Assuming this to be the surface of pure carbon, the third  $sp^2$  orbital does not participate in  $\sigma$  bonding, because there is nothing to which it can bond. The  $sp^2$  orbital not participating in bonding to adjacent atoms is called a dangling bond. It represents a particularly reactive site. Differences in reactivity also occur between different types of edge carbon atom. Two kinds of edge site exist, called zigzag and armchair, shown in Figure 19.7. Zigzag edges have higher reactivity than armchair edges, because the  $\pi$  electrons on zigzag carbon atoms delocalize more easily than those on armchair carbon atoms.

All real carbons have surfaces that show various irregularities, such as crystal defects, pores, holes, and cracks. Such defect sites usually have carbon atoms with dangling



On edge carbon atoms, one of the  $sp^2$ orbitals does not participate in  $\sigma$ -bonding. That orbital contains an unpaired electron, sometimes called a "dangling bond."

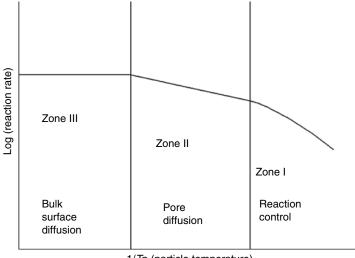
**Figure 19.6** On edge atoms, one of the three  $sp^2$ -hybridized orbitals does not participate in  $\sigma$ -bonding, because there are no atoms to which it can bond. That orbital contains an unpaired electron, sometimes called an unfulfilled valency or a dangling bond.



**Figure 19.7** Surface sites on large planes of carbon atoms can be arrayed as zigzag structures (shown on left) or armchair structures (shown on right). The heavy bold lines denote the two kinds of structure. The squiggles represent bonding of the fragment shown into a much larger carbon structure.

bonds, and can be sites of increased reactivity. Further, real carbons (and coal and biomass) display various degrees of porosity. Gaseous reagents penetrate the pore system and react at interior surfaces. The extent of porosity and the size distribution of pores can be very important in determining overall reactivity, because up to 90% of the total surface area can be internal pore surfaces. Regardless of the specific reactant, a five-step mechanism usually governs reactions of carbons, the Langmuir–Hinshelwood mechanism, as introduced in Chapter 13. In principle, any of the five steps of the Langmuir–Hinshelwood mechanism can be rate-determining. Often, but not always, the rate-determining step is the third step, reaction on the carbon surface. In such a case the rate depends on the usual parameters: temperature, pressure, and particle size. Rate also depends on properties of the carbon, such as active site concentration, porosity, and the possible presence of impurities that could catalyze the reaction.

Gasification rate depends on temperature. Assuming a completely non-porous carbon, at low reaction temperatures the rate-determining step is chemically controlled, i.e. step three of the Langmuir–Hinshelwood mechanism. At high temperatures reaction on the surface is usually fast enough for the rate to be under diffusion control, so the rate-determining step is mass transport of the reactant molecules to the surface. Virtually all real carbons, coals, and biomass solids possess some porosity. Porosity provides the potential for an intermediate type of reaction, in which rate is chemically controlled over the external surface, but reaction on the internal surfaces is limited by diffusion. The diffusion limitation may be that of diffusion of reactants through the pores to the reactive internal surfaces, diffusion of products outward through the pores, or both. Because of these considerations, gasification reactions are divided into three temperature zones: Zone I occurs at low temperatures where reaction rates are usually low. Chemical control of the reaction exists over the entire surface. The concentration of



1/Tp (particle temperature)

**Figure 19.8** This plot of reaction rate as a function of reciprocal temperature (an Arrhenius plot), illustrates three reaction zones in gasification reactions. A different effect controls the rate in each zone.

gas inside the bulk of the carbon is the same as it is in the gas phase. Low temperature, low pressure, and small particle size result in a reaction being in Zone I. Zone II represents the intermediate region, in which diffusion in the pores partly controls the overall rate. Inside the carbon particle, the reactant concentration decreases until it goes to zero at some point. In Zone III, diffusion of gaseous reactant to the carbon surface controls the rate. A boundary layer exists in which the reactant gas concentration is lower than it would be in the bulk gas phase. An Arrhenius plot of log rate as a function of 1/T would look like that shown in Figure 19.8.

Following the concentration of the reactant gas in the gas phase and in the carbon provides an alternative illustration of the differences between the three reaction zones (Figure 19.9).

Interaction of an oxygen molecule with the carbon surface begins with chemisorption, as sketched in Figure 19.10, or dissociative chemisorption, in which the diatomic molecule breaks apart as shown in Figure 19.11.

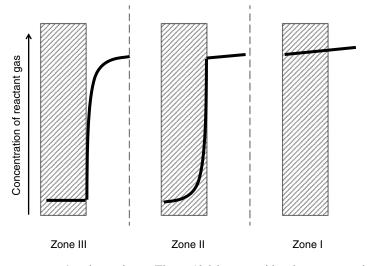
The adsorbed species might be fixed to a specific surface active site, or could be mobile on the surface. In the reactions that follow, chemisorbed species are denoted in parentheses, e.g. C(O). The subscript m denotes surface species that are mobile, e.g.  $C(O)_m$ , and an asterisk denotes a carbon atom that is an active site.

The carbon–oxygen reaction begins with an oxygen molecule physisorbing to the carbon surface, breaking the O–O bond, and forming a pair of chemisorbed oxygen atoms, or a pair of loosely held and mobile oxygen atoms, or one of each:

 $C(O_2)_m \rightarrow C(O) + C(O) \quad \text{or} \quad C(O)_m + C(O) \quad \text{or} \quad C(O)_m + C(O)_m.$ 

Either the chemisorbed or loosely held oxygen atom can form carbon monoxide,

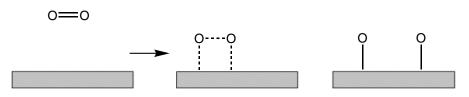
$$C(O) \rightarrow CO$$
 and  $C(O)_m \rightarrow CO$ .



**Figure 19.9** An alternative to Figure 19.8 is to consider the concentration of a reactant gas in the gas phase and in the interior of a particle of carbon. In Zone I, the concentration in the interior is the same as in the bulk gas. In Zone II, limitations on diffusion of the gas in the pores of the carbon cause the concentration to drop as the gas penetrates the carbon. In Zone III, reaction occurs so rapidly that gas concentration drops near the surface, but then is constant inside the particle.



**Figure 19.10** Oxygen can interact with carbon particles by chemisorption, formation of a weak chemical bond between the oxygen molecule and surface atoms.



**Figure 19.11** Oxygen can also interact by dissociative chemisorption, which results in cleavage of the oxygen molecule, and formation of bonds between individual oxygen atoms and surface atoms.

Mobile, loosely held oxygen atoms, or a mobile oxygen and chemisorbed oxygen, interact to produce carbon dioxide and leave behind a new carbon active site,

$$C(O)_m + C(O)_m \rightarrow C^* + CO_2$$
 and  $C(O)_m + C(O) \rightarrow C^* + CO_2$ .

Gas-phase carbon monoxide can react with a site having a chemisorbed oxygen atom to produce carbon dioxide and a carbon active site; the same reaction can occur with a loosely held, mobile oxygen:

$$CO + C(O) \rightarrow C^* + CO_2,$$
  
 $CO + C(O)_m \rightarrow C^* + CO_2.$ 

Oxygen in the gas phase can interact with chemisorbed oxygen sites, also producing carbon dioxide:

$$O_2 + 2 C(O) \rightarrow 2 CO_2.$$

Carbon reacts with carbon dioxide in the Boudouard reaction. Two mechanisms have been proposed. Carbon dioxide can react with carbon to produce carbon monoxide and a site having a chemisorbed oxygen atom:

$$C + CO_2 \rightarrow C(O) + CO.$$

Or, the site containing chemisorbed oxygen forms carbon monoxide, leaving behind a newly generated active site:

$$\mathbf{C}(\mathbf{O}) + \mathbf{C}\mathbf{O} + \mathbf{C}^*.$$

And, carbon monoxide can chemisorb to the carbon active site:

$$C^* + CO \rightarrow C(CO).$$

Alternatively, the carbon–carbon dioxide reaction is followed simply by conversion of a chemisorbed oxygen atom to carbon monoxide and a carbon active site:

$$C + CO_2 \rightleftharpoons C(O) + CO_2$$
  
 $C(O) \rightarrow CO + C^*.$ 

The unusual feature of the Boudouard reaction is its inhibition by carbon monoxide. Inhibition results from adsorption of CO on carbon active sites.

The carbon-steam reaction is

$$C + H_2O \rightarrow CO + H_2$$
,

for which two mechanisms have been proposed. One involves formation of a surface oxygen complex by reaction with water, its conversion to carbon monoxide, and reaction of the hydrogen with a carbon active site:

$$C + H_2O \rightarrow C(O) + H_2,$$
  
 $C(O) \rightarrow CO,$   
 $H_2 + C^* \rightarrow C(H_2),$ 

or, reaction of water on a carbon active site, and decomposition of the carbon–oxygen surface complex:

$$C^* + H_2O \rightarrow C(O) + H_2,$$
  
 $C(O) \rightarrow CO.$ 

The carbon-hydrogen reaction has particular interest when the objective of gasification is to produce methane, i.e. substitute natural gas. Synthesis gas is converted to methane downstream of the gasifier. However, high yields of methane directly from the gasifier help the overall process. The reaction is

$$C + 2 H_2 \rightarrow CH_4.$$

A mechanism is proposed to be

$$\begin{split} & C + H_2 \to C(H_2), \\ & C(H_2) + C^* \to 2 \quad C(H), \\ & 2 \ C(H) + H_2 \to 2 \quad C(H_2), \\ & 2 \ C(H_2) + 2 \ H_2 \to 2 \ CH_4 + 2 \ C^* \end{split}$$

In this reaction, the carbon active site is thought to be the group

-CH=CH-,

sometimes incorrectly called a "methylene" group. (The actual methylene group is  $-CH_2-$ .)

The next section focuses on industrial gasification processes. In translating the fundamental chemistry of carbon reactions just discussed into practice, two awkward facts must be addressed: the feedstock is not really pure carbon, and the carbon–steam reaction is endothermic.

#### 19.3.2 Coal gasification processes

Gasification of coal has a very long history, back to the 1790s at least. Before World War II, the United States alone had about twenty thousand small coal gasifiers, making producer gas for domestic use or process heat. Gas made in this way was a popular fuel gas in the United States until the spreading of the interstate natural gas pipeline network in the years after World War II. Many of the processes were simple pyrolysis or steam-carbon reactions in relatively crude equipment and having serious environmental problems. Beginning in the 1930s and continuing thereafter, the interest in large-scale gasification shifted to production of synthesis gas to make substitute natural gas or synthetic liquid fuels. This led to much more sophisticated processes, particularly combining the steam-carbon reaction with the simultaneous combustion reaction, operation at high pressure, and use of O2 instead of air. All of the approaches to coal gasification developed in roughly the last 60 years represent different designs for carrying out the carbon-steam-oxygen or carbon-steam-air reaction and for balancing the various exothermic and endothermic reactions. Nowadays there is increasing interest in applications of biomass or solid wastes as feedstocks.

The key to today's successful large-scale gasification technology lay in the realization that steam and air (or oxygen) could be reacted with coal simultaneously, analogous to partial oxidation. By appropriate selection of the ratio of these feeds, the exothermic incomplete combustion reaction balances the endothermic carbon-steam reaction making the net process thermally neutral, or perhaps slightly exothermic. Gasifiers in which the oxygen is supplied directly from air are called air-blown units. However, the oxygen is diluted with four times its volume of nitrogen. Nitrogen plays little or no role in the chemistry, but is a nearly-inert diluent that, sooner or later, has to be separated from the eventual products, and has a number of disadvantages. Compressing air for the gasifier, or compressing gases for downstream processing, wastes considerable energy in compressing nitrogen that eventually will be returned to atmospheric pressure. Carrying nitrogen through the process requires larger vessels and piping downstream, to accommodate the additional volume; these require greater capital investment because of their larger size. Feeding oxygen instead of air to the gasifier eliminates these problems, but brings a new one – the additional capital and operating expense for an air separation unit upstream of the gasifier. As gasifier designs have evolved and commercial-scale operating experience has been accumulated, the balance between these conflicting advantages and disadvantages has come strongly to favor oxygen-blown gasifiers.

High-pressure operation enhances formation of methane by favoring the right-hand side in the reaction  $C + 2 H_2 \rightarrow CH_4$ . If production of methane is the ultimate objective, increased yields of methane from the gasifier itself reduce the requirements on the water-gas shift unit (Chapter 20) to achieve the desired 3:1 H<sub>2</sub>:CO ratio in the gas used for methane synthesis. High-pressure operation also reduces or eliminates the need for downstream compression of the product gas before it can enter the distribution pipelines.

Temperature can be controlled to be below the melting point of the ash (Chapter 18), so that ash is removed as a solid. Normally, temperature control is effected by running with excess steam. Gasifiers that operate in this way are called dry-bottom, or dry-ash, gasifiers. They are dry in the sense that the ash is not a molten liquid, but in many designs the hot ash is quenched in water, so that the ash being removed actually resembles wet mud. Alternatively, the temperature can be controlled so that the ash melts as it forms, and is removed as a liquid. Such units are called slagging gasifiers, or sometimes "slaggers."

At least five reactions are likely inside a gasifier, as introduced previously. Each is reversible. None of the reactions involved in gasification proceed at appreciable rate until temperatures above 800 °C are reached. These same reactions apply equally to gasification or partial oxidation of other feedstocks, including biomass, oil from oil sands, or petroleum coke. All approaches to commercial, large-scale gasification processes developed in the past 80 years represent different tactics for carrying out the carbon–steam and carbon–oxygen reactions simultaneously and appropriately balancing the various endothermic and exothermic reactions. The composition of the product gas depends on factors related to the design and operating procedures for the specific gasifier, including the balance between the five reactions shown previously, and whether or not the feedstock was heated slowly through thermal decomposition, which would add an assortment of hydrocarbon species to the product. In principle, another factor could be whether the gasifier was air-blown or oxygen-blown, but that issue has largely vanished with the dominance of oxygen-blown units.

As discussed below, some gasifier designs have relatively long residence times and slow heat-up, so that the feedstock has an opportunity to undergo pyrolysis before encountering gasification conditions. Pyrolysis drives off a variety of volatile organic products; some of these might undergo thermal cracking reactions inside the gasifier. When that happens, additional methane appears in the products, formed via the generic reaction

$$C_xH_y \rightarrow \frac{y}{4}CH_4 + (x-\frac{y}{4})\,C.$$

This reaction provides yet another example of internal hydrogen redistribution to form a hydrogen-rich product and a carbon-rich product from the original feedstock.

Gasification has two major uses. One is burning the *cleaned* product gas in a combustion turbine as part of an IGCC plant, as discussed above. The other is to use the carbon monoxide/hydrogen synthesis gas for production of methane (substitute natural gas), methanol, liquid hydrocarbon fuels, or chemicals; this is the topic of Chapter 21. A third application that may emerge is to "shift" the gas composition all the way to hydrogen. Currently, hydrogen production is dominated by hydrogen made from steam reforming of natural gas. In the future, coal gasification may have a role in this market, sometimes referred to as "hydrogen from coal" [B]. Biomass gasification to produce hydrogen represents a route to renewable hydrogen, with, in principle, no carbon emissions, since any  $CO_2$  produced would be considered to be absorbed by the next year's crop of biomass.

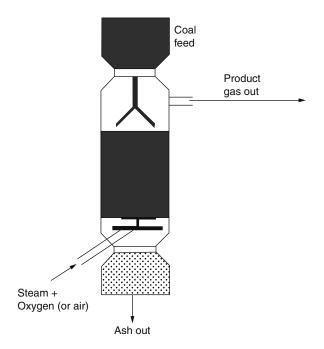
#### 19.3.3 Fixed-bed gasification

The most successful gasifier design to date is the fixed-bed gasifier. The name may be slightly misleading; what is actually "fixed" is the height of the bed, not the position of an individual feedstock particle. During reaction, a particle moves downward through the gasifier until eventually it is consumed. (For this reason, these same units are sometimes referred to as moving-bed gasifiers.) Fresh feed is added continually at the top of the gasifier, maintaining the height of the bed. Figure 19.12 is a conceptual diagram of a generic fixed-bed gasifier.

All fixed-bed gasifiers in commercial operation are dry-ash units, sometimes known as fixed-bed dry-bottom (FBDB) gasifiers. Operating temperatures of FBDB gasifiers are limited by the fusion temperatures of the ash (Chapter 18). Operating temperatures would be in the range 950–1050 °C. Some advantages accrue by operating at much higher temperatures [C], as a slagging fixed-bed gasifier.

FBDB gasifiers typically operate at 3–4 MPa; all major commercial units currently use coal as feedstock. Because of the elevated operating pressure, coal must be introduced, and ash withdrawn, via special locks somewhat analogous to the air locks on spacecraft. A distributor smooths the coal so that the height of the bed is more-or-less even across the gasifier. Despite the added mechanical complexity, extra capital investment, and added maintenance of the coal and ash locks, pressurized operation provides several advantages relative to operating at ambient pressure: a greater throughput per size of vessel; reducing or eliminating downstream gas compression; and shifting the hydrogenation equilibrium to favor methane formation, desirable when the plant is designed to produce substitute natural gas.

Coal entering an FBDB gasifier is heated by hot gases ascending from the grate region. First, moisture is driven off. Then, as the dried coal descends further and its temperature increases, it begins to experience pyrolysis, during which a wide variety of organic compounds is driven off. The moisture and the organics are condensed



**Figure 19.12** A fixed-bed gasifier. Coal is fed through a lock-hopper and gradually descends through the shaft as it is consumed near the grate. Ash is removed through a second lock-hopper. The raw product gas usually contains condensable vapors of tars and suspended fine particles of coal or ash.

downstream of the gasifier, forming an aqueous liquor containing various polar compounds such as phenols, and forming a complex organic mixture called tar. The liquor could contain other soluble products of the thermal decomposition of coal, such as ammonia and hydrogen sulfide. Finally, the coal char descends into the region where the carbon-steam and carbon-oxygen reactions occur. The bottom-most zone of the gasifier is the combustion zone, where the principal reaction is the carbonoxygen reaction, supplying heat for the endothermic carbon-steam reaction. The carbonaceous material is consumed entirely, leaving the ash to be withdrawn through the ash lock. The residence time of a given coal particle is approximately an hour. The gas composition depends on the composition of the coal feed and the steam:oxygen ratio. After removal of impurities such as hydrogen sulfide, ammonia, and tars, gas produced from bituminous coal has a composition of about 40% hydrogen, 30% carbon dioxide, 20% carbon monoxide and 10% methane. When excess steam is used to help keep the temperature below the onset of slag formation, some of the steam shifts the equilibria in the carbon-steam and water gas shift reactions to favor more hydrogen production.

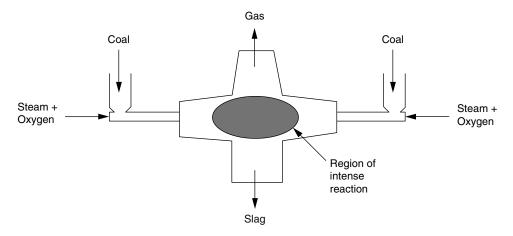
Raw gas leaving the gasifier is not used directly as a fuel. Rather, it undergoes a variety of clean-up operations, depending on its eventual intended use. In addition, the ratio of carbon monoxide to hydrogen might be "shifted," again depending on what will be done with the gas. These treatment and shifting operations are discussed in Chapter 20. While FBDB gasifiers enjoy considerable commercial success worldwide, they cannot operate well on caking coals. Measures can be taken to destroy the caking properties of the coal before gasification, or to try to break up the agglomerated masses of coal by having a stirrer in the bed. The caking propensity of the coal can be reduced, or destroyed completely, by mild oxidation prior to the coal being fed to the gasifier. These gasifiers also cannot handle fine coal of size <0.6 mm (below about -28 mesh). The latter problem can be resolved by co-locating a gasification facility and an electric power station that uses pulverized-coal-fired boilers. Coal too fine to be gasified can be sent to the power plant, and coal too coarse to be burned goes to the gasification plant. While these gasifiers have some limitations, they also have some advantages. Moisture is not a problem. Lignites with  $\approx$ 30% moisture can be run successfully. The ash value is not a significant limitation, with successful operation on coals >35% ash, provided that care is taken to avoid agglomeration into large clinkers, or outright slagging.

Although other reactor designs about to be discussed can claim advantages vis-à-vis the FBDB gasifiers, or claim not to suffer some of the disadvantages, one advantage of the FBDB units that is difficult to trump is their long history of successful operation at a commercial scale. Gasifiers that are evolutionary descendants of the original Lurgi fixed-bed gasifier, which dates from the 1930s, are in use in synthetic fuel plants in South Africa and in the substitute natural gas plant in North Dakota in the United States.

### 19.3.4 Fluidized-bed gasification

In fluidized-bed gasifiers, a steam/oxygen mixture is injected into the bottom, passing upward through a bed of pulverized coal. The flow rate of the steam/oxygen mixture is high enough to lift, or fluidize, the coal particles. The steam/oxygen mixture not only fluidizes the coal particles, but also reacts with the coal at the same time. Fluidization of the bed allows excellent mixing and contacting of the reacting gases with the solid particles. The mixing also helps maintain uniform bed temperature. Like fixed-bed units, fluidized-bed gasifiers have difficulty handling caking coals. As the coal begins to cake, the coal particles agglomerate to a size at which they cannot be fluidized, consequently falling out of the bed. Agglomeration of ash particles leads to a similar problem. Very fine particles, such as inherent mineral matter liberated as the carbon gasified, or small particles of coal not yet completely gasified, can become entrained in the flowing gas mixture and swept out of the reactor. A solid/gas separation unit is needed downstream of the gasifier to remove these solid particles.

The most successful fluidized-bed gasifier, on a commercial scale, is the Winkler gasifier, which was developed in the 1920s. The Winkler design started as an air-blown, atmospheric pressure gasifier. Motivation for development was to have a unit capable of utilizing coal fines, considered a waste product by operations utilizing lump coal and therefore often cheaper than lump coal. The Winkler operates at about 950 °C, with residence times up to three hours. It is difficult to handle a caking coal in a Winkler gasifier, and the relatively low temperature also makes it hard to run coals of low reactivity, such as anthracites. Winkler units only work well on low-rank coals. A so-called high-temperature Winkler gasifier, which really is a high-*pressure* unit, has been tested successfully in demonstration plants of capacities of several hundred tonnes per day, and is under consideration for use in IGCC applications.



**Figure 19.13** Schematic diagram of a two-headed Koppers-Totzek gasifier. Pulverized coal is blown into the central reaction chamber. Temperatures are high enough to assure very short residence times, and to assure melting of the ash, allowing its removal as a molten slag.

#### 19.3.5 Entrained-flow gasification

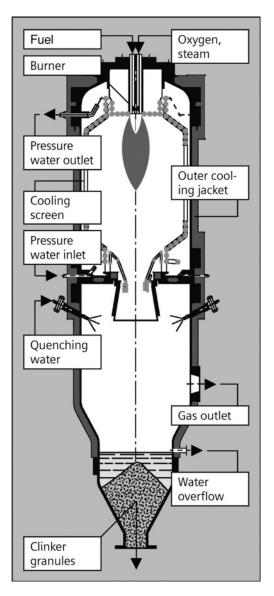
Entrained-flow gasifiers operate by entraining particles of coal in a stream of steam, oxygen, or both. Successful operation requires very fine particle sizes of coal, typically of the order of 75  $\mu$ m. Among the major types of gasifier, entrained-flow units operate at the highest temperatures. As consequences: entrained-flow gasifiers operate as slaggers; they produce less methane than other units (an advantage if the intent is to produce synthesis gas for making hydrogen or liquid fuels); and they produce the lowest H<sub>2</sub>:CO ratio, implying the need for a greater amount of downstream gas conversion if methane or hydrogen is the desired product of the plant.

Residence times are very short, no more than a few seconds. The feed coal does not have time to pyrolyze, so by-product tars do not form. Also, the coal does not have time to pass through the plastic state associated with caking behavior. Handling caking coals is not a problem. Because the reaction temperatures are so high, coals of any rank and virtually any degree of reactivity can be used as feeds.

The Koppers–Totzek (K–T) gasifier is shown in Figure 19.13. The design, with two injection systems diametrically opposed, is called a two-headed K–T gasifier.

Four-headed designs, with four injection systems arrayed 90° apart around the circumference of the gasifier, are also in use. These gasifiers operate at atmospheric pressure. Reaction temperatures may be  $\geq 1600$  °C. Residence time of a coal particle is  $\approx 1$  s. Any rank of coal can be used as feedstock. The very high reaction temperatures melt the ash, which is removed as a slag. The K–T product gas is 55–60% CO, 30% H<sub>2</sub>, 10% CO<sub>2</sub>. Disadvantages include the need for downstream compression work, very high oxygen consumption, and the need either to recover, or to tolerate the loss of, the sensible heat in the product gas, which can exit the gasifier at 1350–1400 °C.

K–T gasifiers have been in commercial use in several countries in Europe, Africa, and India. A major application is production of hydrogen for subsequent ammonia synthesis, the ammonia being used for fertilizer production. The K–T gasifier has largely been superseded by the Shell gasifier; new K–T units have not been built in some years.

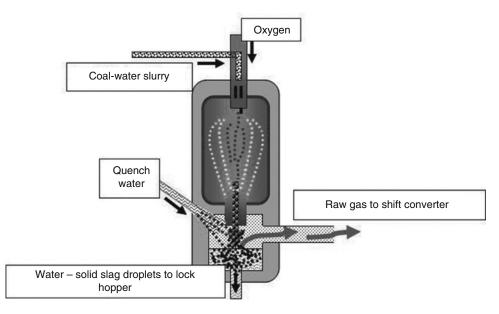


**Figure 19.14** Entrained-flow gasifiers operating on pulverized fuel usually fire the fuel, steam, and oxygen downward. High temperatures provide short residence times and slagging operation.

The Shell gasifier (Figure 19.14) is a pressurized version of the K–T, operating up to about 3 MPa.

This gasifier is in successful commercial operation in several European countries, as well as Brazil and Malaysia. Most run on vacuum distillation resid rather than coal; the dominant applications are for synthesis of ammonia, methanol, or both.

In several respects the General Electric gasifier, originally developed by Texaco, combines the high reaction rates and the lack of by-product tars of the K–T gasifier, with the advantages of pressure operation. This process for gasification derives from the



**Figure 19.15** The GE–Texaco gasifier is similar to that shown in Figure 19.14, but uses a slurry of coal in water as the feed, rather than pulverized solid coal.

Texaco partial oxidation process, described above. Feeding coal as a slurry in water eliminates mechanical problems of the pressure locks in typical FBDB gasifiers. Introducing a liquid into a pressure vessel by pumping it to the desired pressure is easier than trying to get a solid into a pressure vessel. The solids loading in the slurry is up to 70%.

The General Electric gasifier (Figure 19.15) is a cylindrical steel shell with a refractory lining. It consists of two main sections, one for gasification, and the other for quenching the slag. Coal:water slurry and oxygen are fed into the top. Because residence time is of the order of a few seconds, coal is consumed immediately without production of by-product tars (or, if any tar components do form, they are promptly consumed). The high temperatures result in the ash melting to form slag, which is solidified in the quench section, and removed via an ash lock. This gasifier operates in the range 2–9 MPa at temperatures of 1100–1350 °C. Higher temperatures would be likely to damage the refractory lining.

A typical product gas has a composition 45–50% carbon monoxide, 35% hydrogen, and 15% carbon dioxide. Heating rate in the General Electric gasifier is so high that the coal does not have time to display caking behavior. Care must be taken with coals of low rank, and therefore of low calorific value, to ensure that enough heat can be generated from the coal to evaporate the water coming into the gasifier with the slurry.

### 19.3.6 Underground coal gasification

The notion of gasifying coal in its seam underground, completely eliminating mining and transportation of solid coal, goes back to about 1870. The first proponent was Sir William Siemens [D], in Britain. About 20 years later, the idea was championed by Dmitri Mendeleev [E] in Russia. Mendeleev's ideas may have influenced Lenin, who further promoted the concept around the time of the Bolshevik revolution as a means of freeing Soviet laborers from the drudgery and danger of underground coal mining. The Soviet government took up the cause in the 1930s. For many decades the former Soviet Union was the world leader in underground coal gasification (UCG) technology. At various times in the twentieth century, Britain, the United States, Canada, and several European countries proceeded with UCG development in fits and starts, usually in times of "energy crises" when natural gas was perceived to be in short supply or to be too expensive. Often these programs were scaled back when gas prices and availability returned to acceptable levels.

The basic principles of UCG are exactly the same as more conventional, above-ground gasification processes. To operate a UCG process, a minimum of two wells must be bored into the coal seam, an injection well for supplying air and possibly steam, and a production well for removing the gas produced. These wells must be linked, either through the natural porosity and permeability of the coal in the seam, or through a connecting channel bored between the two wells. Injection of air initiates the combustion reaction. As combustion proceeds, coal ahead of the combustion front gets hot enough to allow the Boudouard reaction of coal with carbon dioxide produced in combustion. If the coal has high moisture content, or if steam is injected with air, the carbon–steam reaction also occurs. Some tars produced from pyrolysis of the coal could crack to light hydrocarbons.

By eliminating costs and temporary environmental degradation associated with coal mining, and the cost of transporting coal, it would seem that UCG could be a less expensive technology than above-ground gasification. Further, there is no need for the capital expense of the gasifiers, coal crushing and handling equipment, or downstream clean-up equipment. Another advantage of UCG is that it could, in principle, be applied to conversion of coal in seams that are either too deep, or that pitch at too great an angle, to be mined at all. Several issues offset these perceived advantages. UCG technology development to date has relied heavily on air-blown technology, so that the product gas is highly diluted with nitrogen and its calorific value is low (about  $6 \text{ MJ/m}^3$ ). Above-ground gasifiers can be of standardized designs, modified only slightly to accommodate the characteristics of the specific feedstock. UCG installations are more likely to be one-off designs, customized to fit the local geology. Groundwater could become contaminated by organic compounds formed during coal pyrolysis, and by various inorganic compounds liberated as the coal is consumed. Some of these contaminants pose problems for environmental quality or human health. Water could also percolate or flow into the gasification zone, reducing the temperature and possibly stopping the process. These issues with water are of particular concern when the UCG system is operating below the natural water table, as is often the case. Even a process that was a complete success and gasified completely a thick coal seam could result in subsidence of the ground above. Aside from the potential property damage to surface structures, subsidence could sever the link between production and injection wells, and could allow gas to escape to the surface.

#### 19.3.7 Biomass gasification

Recent years have seen increasing interest in biomass gasification, or in the co-gasification of biomass and coal. Several issues provide motivation. For most countries, biomass is a domestic resource that can be controlled by national policy, and not subject to the geopolitical and macroeconomic issues of oil importation [F]. Biomass is thought to be a renewable resource on human time scales, whereas the fossil fuels definitely are not. Biomass can be considered to be carbon-neutral, or nearly so, meaning that the carbon dioxide emitted from its use is, in principle, recaptured in growing the next year's crop.

To a large extent, biomass gasification resembles coal gasification, with some distinctions that take into account the particular differences between biomass and coal. The kinds of biomass usually considered for gasification include wood, wood wastes (e.g. sawdust), and municipal solid wastes. Some kinds of grass, such as switchgrass (*Panicum virgatum*), grown as energy crops might also serve as feedstocks. Rather broadly, relative to coal, biomass usually has lower calorific value, lower sulfur content, higher moisture content, higher amounts of hydrogen and oxygen, and produces a higher yield of volatiles on pyrolysis. Biomass does not have the caking properties of bituminous coals, so its gasification is not limited – at least on this basis – to systems able to handle caking feedstocks. Generally biomass chars are more reactive than coal chars, so it may prove that less steam and oxygen are needed for biomass gasification relative to coal.

Coals generally are brittle solids, while biomass tends to be fibrous. This distinction affects the feed preparation and feeding systems. Coals can be crushed and ground to reach desired small particle sizes. Biomass, however, has to be shredded. A facility gasifying both kinds of feed requires two sets of preparation equipment. Changes to the feeding system may be needed to convert a gasifier design from coal to biomass or biomass/coal mixtures as the feedstocks.

### Notes

- [A] This reaction is named in honor of the French chemist Octave Boudouard (1872–1923), who studied the position of equilibrium in this system in the early years of the twentieth century. Boudouard collaborated closely with Henri Le Chatelier, including their jointly written book, *High-Temperature Measurements*. At least two streets in France are named in Boudouard's honor, one in Paris (in the Corbiel Essones area), and the other in Jussy, Aisne.
- [B] If one examines carefully the stoichiometry of the various gasification reactions, this term is misleading. Most of the hydrogen produced from coal gasification is not *from* coal. Rather, coal serves as the reducing agent for splitting water molecules to hydrogen. As is always true in reduction–oxidation reactions, the reducing agent becomes oxidized, mainly to carbon monoxide. Most of the hydrogen made in such a process is from steam.
- [C] High-temperature operation gives improved kinetics, resulting in higher throughputs of coal in the plant. Thus more gas can be made in a given time for a set size of gasifiers, or alternatively, smaller gasifiers would be needed to meet a desired gas output. This advantage is counterbalanced by several considerations. Materials used in gasifier construction, i.e. alloys or refractories, need to be selected for hightemperature service. And, care must be taken to avoid slagging in a dry-bottom gasifier, or to keep the slag flowing in a slagger.
- [D] Sir William Siemens (1823–1883) was a German-born mechanical engineer who spent much of his career in England. In a full and active life, Siemens pursued research and development in many fields, including metallurgy and electrical

engineering. His most enduring invention is the open-hearth furnace used in steel making, in what is nowadays known as the Siemens–Martin process.

- [E] Dmitri Mendeleev (1834–1907) is best known today as the person who developed the periodic table of the elements. He was involved in much more than that, including studies of the composition of petroleum, being involved in establishing the first oil refinery in Russia, ideas of the abiogenic origin of hydrocarbons (from metal carbides formed deep inside the earth), and development of new standards for production of vodka. Attempts to nominate Mendeleev for the Nobel Prize in chemistry were blocked by the implacable opposition of Svante Arrhenius, nursing a long-held grudge because Mendeleev had been critical of his theory of dissociation of ionic compounds in solution.
- [F] Another issue helps to ensure that biomass is a domestic energy resource. Though estimates vary somewhat, it is generally considered that it is uneconomic to ship biomass more than 50–150 km to reach a processing plant or utilization facility. Barring a drastic change in energy economics, an extensive international trade in raw biomass does not seem likely.

#### **Recommended reading**

- Berkowitz, Norbert. *An Introduction to Coal Technology*. Academic Press: New York, 1979. Chapter 12 of this excellent book reviews gasification technology.
- Higman, Christopher and van der Burgt, Maarten. *Gasification*. Gulf Professional Publishing: Burlington, MA, 2008. An excellent discussion of gasification, including thermodynamics, kinetics, gasification processes, and their applications.
- Lee, Sunggyu. *Alternative Fuels*. Taylor and Francis: Washington, 1996. Chapters 3, 5, and 11 are relevant, treating coal gasification, IGCC plants, and biomass gasification.
- Miller, Bruce G. *Clean Coal Engineering Technology*. Butterworth-Heinemann: Burlington, MA, 2011. Chapter 5 of this comprehensive monograph discusses gasification systems.
- Probstein, Ronald F. and Hicks, R. Edwin. *Synthetic Fuels*. Dover Publications: Mineola, NY, 2006. This Dover edition is a relatively inexpensive paperback reprint of a book originally published in the 1980s. Highly recommended to anyone working in, or interested in, the field of synthetic fuels. Chapters 3, 4, and 8 have material pertinent to the present chapter.
- Rezaiyan, John and Cheremisinoff, Nicholas P. *Gasification Technologies*. Taylor and Francis: Boca Raton, 2005. This book covers approaches to integrating gasification into various systems, such as IGC plants and fuel cell systems, as well as covering gasification principles and reviewing various technologies.

# 20.1 Gas clean-up

Gasification or partial oxidation is likely to be practiced with one of two purposes: to supply gaseous feed for an IGCC plant, or to use the carbon monoxide/hydrogen mixture as synthesis gas. Neither application uses raw gas with no downstream treatment. The desirable components of the product gas are carbon monoxide, hydrogen, methane, and other light hydrocarbons. If the gas were to be used in combustion applications on site, carbon dioxide and water vapor would be considered neutral, i.e. having neither a positive nor negative effect, except for their effect as diluents of the combustible gases. If the gas is to be upgraded, further processed, or shipped by pipeline, then both of these components are undesirable. Processing units would have to be larger to handle these "extra" components that make no contribution to the calorific value of the gas. Some heat and compression work would be wasted on diluents of the desired components of the gas. Components of the raw gas that are always undesirable include particulate matter, droplets of tar, hydrogen chloride, ammonia, and hydrogen sulfide and other sulfur-containing compounds.

A first treatment step involves removal of particulate matter, which may consist of fine particles of ash or of partially reacted feedstock. This can be accomplished using a cyclone separator. Cyclones can be designed to operate at temperatures to 1000 °C, and pressures to about 50 MPa. They work well for particle sizes above 5  $\mu$ m. If it is necessary to remove finer particles, baghouses with fabric filters or electrostatic precipitators can be used.

Raw gas exiting a gasifier has a temperature determined by the kind of unit being used, i.e. whether fixed-bed, fluidized-bed, or entrained flow, and whether it is operated as dry-bottom or slagger. It is likely that the gas will have to be cooled before being treated further. Because this could involve losing some of the sensible heat of the gas, and require more energy if the gas is later to be re-heated, there is interest in developing "hot gas" clean-up methods (discussed below). Indirect heat exchange cools the gas, but at the same time allows generation of some process steam by taking advantage of the the sensible heat in the gas (Figure 20.1).

Alternatively, the gas can be cooled by direct quenching and scrubbing with water, usually in a spray tower, as sketched in Figure 20.2.

Doing so helps to remove any particulate matter, and dissolves water-soluble components of the gas. The gas can be cooled so that water and tars condense. Some heavier components of the tar might even solidify. The condensed sticky liquids in the tar can capture solidified tar components and any solid particles of ash or partially reacted coal

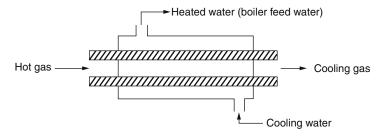
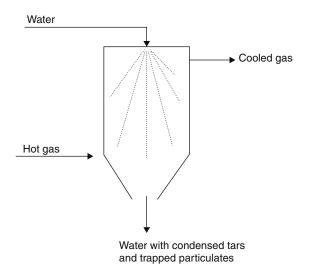


Figure 20.1 A simple shell-and-tube heat exchanger can be used for gas cooling. It may be possible to utilize the same unit to pre-heat boiler feedwater.



**Figure 20.2** In a spray tower, the gas is cooled by direct contact with a water spray. Organic vapors condense to form oils or tars. Particles of coal or ash might be knocked out of the gas stream by the spray.

that were not removed by the cyclone. If water is the only concern, it can be removed by absorption into glycols.

Ammonia is very soluble in water; at ambient pressure and temperature its solubility is about 500 g per liter. Ammonia will dissolve in the water in the spray tower. It is an important industrial chemical, produced at about 110 megatonnes per year and used in fertilizer production. Recovery and sale of ammonia as a byproduct can enhance the economics of a gasification facility. As with any gas, the equilibrium solubility is governed by Henry's Law:

$$P = h x$$
,

where *P* is the partial pressure of the gas and *x* is its mole fraction in solution. The term *h* is the Henry's Law constant, the value of which depends on the nature of the gas and the temperature. From the form of the Henry's Law equation, solubility is inversely proportional to *h*. At 25 °C the Henry's Law constant for ammonia is three orders of magnitude smaller than *h* for hydrogen sulfide or carbon dioxide; consequently, the solubility of ammonia in water greatly exceeds that of these other two compounds.

The solubility equilibria can be written as

$$NH_3(g) \rightleftharpoons NH_3(aq),$$
$$CO_2(g) \rightleftharpoons CO_2(aq),$$
$$H_2S(g) \rightleftharpoons H_2S(aq).$$

In aqueous solution these substances ionize:

$$NH_3(aq) + H_3O^+ \rightleftharpoons NH_4^+ + H_2O,$$
  

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-,$$
  

$$CO_2(aq) + 2 H_2O \rightleftharpoons H_3O^+ + HCO_3^-,$$
  

$$H_2S(aq) + H_2O \rightleftharpoons H_3O^+ + HS^-.$$

In a practical situation

$$NH_4^+ + HS^- \rightarrow NH_4HS$$
,  
 $NH_4^+ + HCO_3^- \rightarrow NH_4HCO_3$ .

When a gasification system contains all three gases – ammonia, hydrogen sulfide, and carbon dioxide – the solubilities of hydrogen sulfide and carbon dioxide can be well above the values predicted from Henry's Law, because of the formation of ammonium hydrogen sulfide and ammonium hydrogen carbonate.

## 20.2 Acid gas removal

Hydrogen sulfide and carbon dioxide are collectively known as acid gases. Several strategies have been developed for acid gas removal. Absorption into a liquid, the most important technique, can occur by simple physical dissolution or by dissolution accompanied by reaction. A variety of proprietary processes has been developed for doing this, all based on countercurrent flow of the gas and the absorbent, followed by some scheme for regenerating and recycling the absorbent. Running at low temperature, high pressure, or both, facilitates absorption. Several such processes are discussed below. Adsorption on a solid might involve an adsorbent such as activated carbon. Because adsorption is a surface process, it is proportional to surface area. Large amounts of finely powdered adsorbent might be needed, potentially making this process impractical for implementation on a large scale. Alternatively, absorption with reaction on solid can be used. This strategy represents an approach to hot gas clean-up. H<sub>2</sub>S can also be destroyed in various chemical reactions; conversion to elemental sulfur offers the economic benefit of selling the sulfur for, e.g. sulfuric acid production.

The Rectisol process takes advantage of the very good solubility of hydrogen sulfide, carbon dioxide, and some related gases (such as carbonyl sulfide, COS) in cold methanol. In general, the solubility of a gas in a liquid increases as temperature decreases. A virtue of methanol in this application is that desirable components of the gas, such as carbon monoxide, hydrogen, and methane, are relatively insoluble in this liquid, and their solubilities do not change much with temperature. As a result, extremely cold methanol, at about -40 °C, does a good job of dissolving acid gases from a gas stream. Figure 20.3 provides a flow diagram for the Rectisol process.

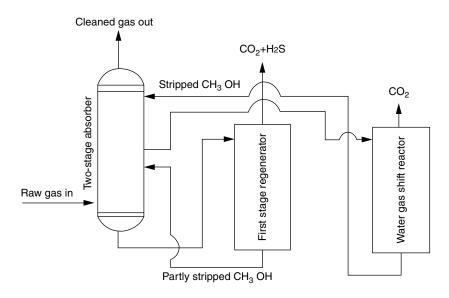


Figure 20.3 Process flow for the Rectisol process.

The Rectisol absorber operates at high pressure and low temperature, typically 5 MPa and -30 to -60 °C, to enhance gas solubility in liquids. The solution of acid gases in cold methanol goes to a regenerator, where pressure is reduced and the methanol is flashed. Lowering the pressure of the gases causes some cooling via the Joule–Thompson effect. The raw gas can also be cooled by heat exchange with the purified gas. Together, these steps help offset some of the refrigeration load, which otherwise would be quite significant. The Rectisol process can usually produce gas of about 10 ppm CO<sub>2</sub> and 1 ppm H<sub>2</sub>S.

The Selexol process also involves dissolution of acid gases, but in this case using glymes as the solvents. Glymes are the dimethyl ethers of various oligomers of ethylene glycol:

CH<sub>3</sub>O–CH<sub>2</sub>–CH<sub>2</sub>–OCH<sub>3</sub>, CH<sub>3</sub>O–CH<sub>2</sub>–CH<sub>2</sub>–O–CH<sub>2</sub>–CH<sub>2</sub>–OCH<sub>3</sub>, CH<sub>3</sub>O–CH<sub>2</sub>–CH<sub>2</sub>–O–CH<sub>2</sub>–CH<sub>2</sub>–O–CH<sub>2</sub>–CH<sub>2</sub>–OCH<sub>3</sub>.

The three compounds shown above are, respectively, glyme, diglyme, and triglyme. The Selexol process offers the advantage, relative to Rectisol, that it requires no refrigeration. Glymes work well as solvents at  $\approx 20$  °C, although there is a difference in solubility by about an order of magnitude in favor of hydrogen sulfide relative to carbon dioxide. A disadvantage is the cost of the solvents, which are quite expensive relative to methanol. The acid gases are removed from solution in the glymes by steam stripping. A flow diagram for the Selexol process is given in Figure 20.4.

The gas leaving the Selexol process contains about 0.5% CO<sub>2</sub> and less than 4 ppm H<sub>2</sub>S.

The Benfield process uses a hot aqueous solution of potassium carbonate at  $\approx$ 2 MPa and 80–150 °C. Two reactions occur:

$$\begin{split} & K_2 CO_3 + O_2 + H_2 O \rightarrow 2 \ KHCO_3, \\ & K_2 CO_3 + H_2 S \rightarrow KHS + KHCO_3. \end{split}$$

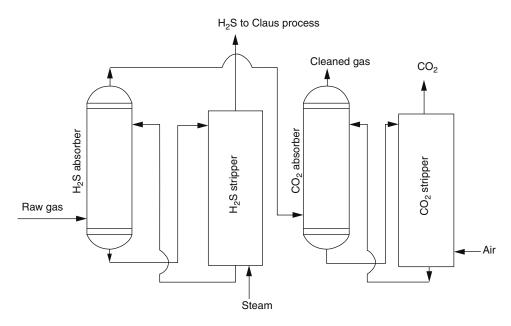


Figure 20.4 Process flow for the Selexol process.

Raw gas flows countercurrently to the potassium carbonate solution in an absorber unit. The process is sketched in Figure 20.5.

The absorber solution can be regenerated by steam stripping. In this process absorption and regeneration take place at about the same temperature, eliminating significant heating or cooling requirements.

None of these processes destroys the acid gases. Rather, they work to concentrate the acid gases for further treatment. The Claus process, introduced in Chapter 10, offers the primary method for dealing with hydrogen sulfide. It relies on two reactions:

$$\begin{split} H_2S + \frac{3}{2}O_2 &\rightarrow H_2O + SO_2, \\ 2H_2S + SO_2 &\rightarrow 2H_2O + 3S. \end{split}$$

The Claus process converts hydrogen sulfide to sulfur. Sulfur potentially can be another valuable by-product of a gasification plant. It finds use in making sulfuric acid, for which annual worldwide production is about 180 megatonnes. Combustion of  $H_2S$  runs as a simple thermal reaction. Reaction of hydrogen sulfide with sulfur dioxide occurs separately in the presence of a catalyst, usually alumina or bauxite, at 200–225 °C. Combustion of  $H_2S$  is strongly exothermic (-15 MJ/kg). Reaction between  $H_2S$  and  $SO_2$  is also exothermic, but to a lower degree, with a reaction enthalpy of about one-sixth that of combustion of  $H_2S$ . A catalyst is used in the second stage to keep reaction rates high. In favorable circumstances the  $H_2S$  concentration in the raw gas stream is high enough so that the total heat liberated from both reactions supplies all the necessary process heat.

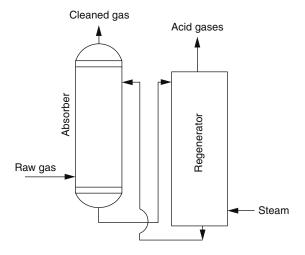
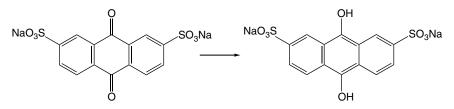


Figure 20.5 Process flow for the Benfield process.

While the Claus process is very effective, it does not reduce the concentration of sulfur-containing gases to zero. The gas leaving the Claus unit, called tail gas, still contains a small amount of sulfur compounds. Whether the tail gas can be vented to the atmosphere or needs to be treated further depends on the environmental regulations affecting a specific plant site. Tail gas from the Claus process can be treated by the Shell Claus offgas treating (SCOT) process, see Figure 20.6. Together, the Claus and SCOT processes recover 99% of the sulfur from the original feed.

The Stretford process also takes sulfur out of the acid gas stream. The reaction employs an oxidation of hydrogen sulfide with sodium metavanadate, followed by regeneration of the oxidizing agent. Regeneration takes place in the presence of added sodium 9,10-anthraquinone-2,7-disulfonate (ADA), which becomes reduced to 9,10-dihydroxyanthracene-2,7-disulfonate (H<sub>2</sub>ADA):



The sequence of reactions is

$$\begin{split} &Na_2CO_3 + H_2S \rightarrow NaHS + NaHCO_3, \\ &4 \,NaVO_3 + 2 \,NaHS + H_2O \rightarrow Na_2V_4O_9 + 4 \,NaOH + 2 \,S, \\ &Na_2V_4O_9 + 2 \,NaOH + H_2O + 2 \,ADA \rightarrow 4 \,NaVO_3 + 2 \,H_2ADA, \\ &2 \,H_2ADA + O_2 \rightarrow 2 \,ADA + H_2O. \end{split}$$

 $H_2ADA$  is converted back to ADA by reaction with air. The entire process runs at temperatures of 40 °C or less. Figure 20.7 provides a flow diagram.

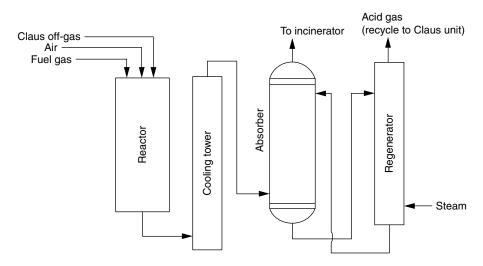


Figure 20.6 Process flow for the SCOT process.

In principle, hydrogen sulfide could be converted completely to sulfur dioxide, and the SO<sub>2</sub> removed, by the well-developed and effective processes used for SO<sub>2</sub> scrubbing from power-plant flue gases. Doing so would produce a very dilute SO<sub>2</sub> concentration, necessitating a large and expensive scrubbing system downstream. Even though SO<sub>2</sub> scrubbers are very good at what they do, it is simpler and cheaper to remove H<sub>2</sub>S from the gas stream in the first place than to incur the extra complexity and cost of making and then removing SO<sub>2</sub>.

Historically, the focus on acid-gas removal has been on hydrogen sulfide; carbon dioxide has been allowed to escape to the atmosphere. This results from the fact that emissions of sulfur-containing gases have been regulated in many countries for decades, whereas carbon dioxide has not. Easy detection of hydrogen sulfide by its characteristic odor also contributes to this focus; anyone – not just those with training in science or engineering – knows immediately that a nearby plant is emitting something noxious. However, the steadily increasing concern about the role of anthropogenic carbon dioxide emissions on global climate change (Chapter 25) suggests that curbs on  $CO_2$  emissions will, sooner or later, be in place. Carbon dioxide capture from an acid-gas removal unit can be effected using various ethanolamines (Chapter 10). With water also present, carbon dioxide reacts as, e.g.,

 $HOCH_2CH_2NH_2 + CO_2 + H_2O \rightleftharpoons HOCH_2CH_2NH_3^+ + HCO_3^-.$ 

Steam stripping of the spent absorber solution produces a CO<sub>2</sub>-rich gas stream. This stream could be fed to a carbon capture and storage system, such as those discussed in Chapter 25. The carbon dioxide concentration in the flue gas of a pulverized-coal-fired power plant would be  $\approx 10-15\%$ ; having a highly concentrated stream that approaches 100% CO<sub>2</sub> from an acid-gas removal unit (or from the water gas shift, discussed below) would make CO<sub>2</sub> capture easier and more effective.

All acid-gas removal processes operate at temperatures substantially below those expected for the raw product gas leaving a gasifier. Cooling the raw gas to 100 °C or below represents the loss of a large amount of sensible heat, though

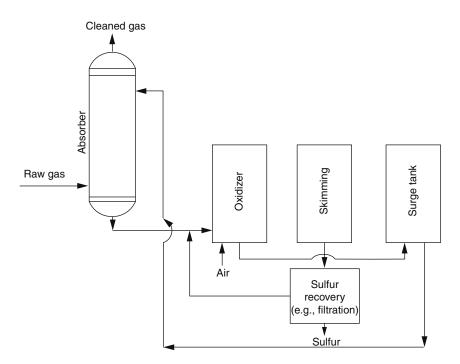


Figure 20.7 Process flow for the Stretford process.

good engineering design would seek to recover much of it via heat exchange. If the gas must then be reheated for further downstream processing, an energy penalty is incurred in this step. Being able to treat the raw product gas without having to cool it would be advantageous. Hot-gas clean-up processes are intended to do this.

Hot-gas clean-up relies on regenerable sorbents that react with hydrogen sulfide. Numerous compounds offer this potential, but iron compounds, where applicable, confer the added bonus of being relatively inexpensive. One such hot-gas clean-up process is based on iron oxide, and involves formation of iron sulfide (shown as "FeS" to denote a non-stoichiometric iron sulfide such as pyrrhotite or mackinawite). Regeneration proceeds via oxidation to magnetite and subsequently to hematite:

 $\begin{aligned} & \operatorname{Fe_2O_3} + 3\operatorname{H_2S} \to ``FeS'' + 3\operatorname{H_2O}, \\ & 3``FeS'' + 5\operatorname{O_2} \to \operatorname{Fe_3O_4} + 3\operatorname{SO_2}, \\ & 2\operatorname{Fe_3O_4} + \frac{1}{2}\operatorname{O_2} \to 3\operatorname{Fe_2O_3}. \end{aligned}$ 

In this scheme, regeneration of the absorbent produces sulfur dioxide. It could be absorbed in a calcium-based scrubber as is used in coal-fired electric power plants. However,  $SO_2$  also has economic potential, if reduced to sulfur or oxidized to sulfuric acid, and in its own right as, e.g. a preservative for dried foods, or a water treatment agent to convert chlorine or its compounds to chloride ion, or as a bleach.

## 20.3 The water gas shift

Composition of raw synthesis gas is affected by two major factors. The first is the H/C ratio of the feed. Chapter 19 introduced generic equations

$$C_n H_m + n H_2 O \rightarrow n CO + (n + \frac{m}{2}) H_2$$
  
 $C_n H_m + \frac{n}{2} O_2 \rightarrow n CO + \frac{m}{2} H_2.$ 

Synthesis gas composition can vary from pure CO (for the partial oxidation of carbon, where m is 0) to a 1:3 ratio of  $CO:H_2$  in the steam reforming of methane. The second factor is the reaction conditions. Temperature and pressure affect the equilibria between the reactions – such as steam–carbon, Boudouard, and shift – that accompany gasification or partial oxidation. The positions of these equilibria in turn impact the gas composition.

As is seen in Chapter 21, requirements for synthesis gas composition are also quite variable. Ammonia synthesis requires pure hydrogen. Methanation to produce substitute natural gas requires a  $H_2/CO$  ratio of 3; methanol synthesis, a ratio of 2. Synthetic fuel and petrochemical industries would find it difficult if a particular application of synthesis gas had to be coupled to a single, very specific feed and set of operating conditions to provide the gas composition necessary for that application. For maximum versatility in configuring processes, some step is needed as an intermediary between the synthesis gas production and use to adjust the  $CO/H_2$  ratio obtained in production to that required for reaction [A]. The intermediate step is the water gas shift (WGS) reaction.

Probably no other equilibrium process is as important in fuel science or engineering as the water gas shift reaction. The reaction can be written as

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{CO}_2 + \mathrm{H}_2.$$

Reacting synthesis gas with steam converts carbon monoxide to dioxide. Absorbing carbon dioxide in, say, monoethanolamine results in a net reduction of the  $CO/H_2$  ratio. Alternatively, reacting synthesis gas with carbon dioxide produces carbon monoxide and water.

The water gas shift can be driven to the right or to the left by applying Le Chatelier's Principle. The number of moles of gaseous product (assuming that water is in the vapor phase) is identical on both sides of the equation, so pressure does not affect the position of equilibrium. The reaction is exothermic when written as

$$CO + H_2O \rightarrow CO_2 + H_2.$$

Usually it is desired to increase the amount of hydrogen. Thus the shift can be run at relatively low temperature, consistent with obtaining reasonable reaction rates. Removing the undesired product helps to shift the equilibrium. To enhance CO formation, water can be removed by, e.g. absorption in glycols (Chapter 10). To enhance  $H_2$  formation,  $CO_2$  can be absorbed in reagents such as the alkanolamines, because it is mildly acidic and is readily absorbed by weak bases. It could also be removed by scrubbing the gas with water at high pressures. The product, after removal of  $CO_2$ , would be essentially pure hydrogen.

Gas	Temperature, degrees C		
	425	810	1027
Carbon dioxide	0.37	0.25	0.13
Hydrogen	0.37	0.25	0.13
Carbon monoxide	0.13	0.25	0.37
Water vapor	0.13	0.25	0.37

**Table 20.1** Effect of temperature on the equilibrium gas composition, in mole fractions, for the water–gas shift reaction.

Since pressure does not affect the position of equilibrium, this takes away a tactic (adjusting WGS reactor pressure) that could be used with Le Chatelier's Principle to help move the equilibrium as desired. More importantly, though, the benefit is that a shift reactor can be run at whatever pressure is most convenient in its role as the intermediary between a high-pressure gasification process upstream and, probably, a high-pressure synthesis process downstream. High-pressure operation, if otherwise feasible, confers the additional virtues of small reactor volume for a given throughput (hence reduced capital cost) and higher reaction rates.

As usually written, with carbon dioxide and hydrogen on the right side, the WGS is exothermic. Thermodynamics indicate that low temperatures would suffice to drive the equilibrium to the right. Unfortunately, reaction rates at low temperatures could be too slow for practical application. Table 20.1 illustrates the effect of temperature on the WGS.

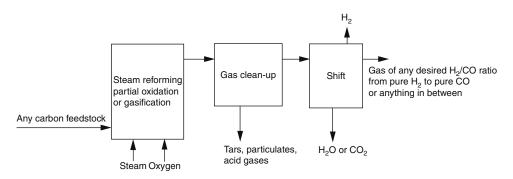
It is not necessary that the entire raw gas stream be shifted to achieve the appropriate  $H_2/CO$  ratio. Starting with a gas having  $H_2/CO$  ratio of x as it comes from the gasifier, and assuming that the gas needed for downstream synthesis would have a ratio of y, the fraction of the gas that needs to be shifted, F, can be determined by straightforward algebra. One can assume a gas composition of 1 mole of CO and x moles of  $H_2$ , the easiest way to have an  $H_2/CO$  ratio of x. After shifting, the gas will have composition 1-F moles of CO and x + F moles of  $H_2$ . The value of the new, desired  $H_2/CO$  ratio, y, will then be

$$y = (x+F)/(1-F),$$

and rearranging to solve for F,

$$F = (y - x)/(y + 1)$$

The shift reaction has been done as a two-stage process in fixed-bed catalytic reactors. (A catalyst does not shift the position of the equilibrium, it only helps attain equilibrium faster.) Reactor pressures are  $\approx 3$  MPa with gas-catalyst contact times of 1 s. The first stage involved an iron catalyst promoted by chromium, typically at 370–425 °C. The second stage used a copper–zinc catalyst at 190–230 °C. Since CO conversion is exothermic, high temperatures reduce its conversion. Lower-temperature operation, e.g. with copper–zinc catalysts, increases the equilibrium constant by a factor of ten. Increasing the amount of steam mixed with the gas fed to the shift reactor provides a convenient way of enhancing the H<sub>2</sub>/CO ratio. These catalysts are poisoned by sulfur, so careful attention must be paid to H<sub>2</sub>S removal upstream of the shift reactor. Use of



**Figure 20.8** A choice of process conditions and hardware can allow conversion of any practical carbonaceous feedstock – fossil and biofuels, or municipal or agricultural wastes – into a synthesis gas of any desired  $H_2/CO$  ratio for later use in synthesis of fuels and materials.

sulfur-tolerant catalysts decreases the need for upstream gas clean-up (Chapter 15). WGS can use a CoMo catalyst on alumina, sulfided before reaction so that the active phase is  $MoS_2$ . Coking, which can be the bane of other catalytic processes, is not a problem in WGS. Excess steam can remove (by gasification) any newly formed carbon. The catalyst lifetime is about three years.

The importance of the WGS is this: by skilful application of Le Chatelier's Principle it is possible to drive the equilibrium to *any* point desired, from pure carbon monoxide to pure hydrogen, or any  $H_2/CO$  ratio in between. Thus the power and versatility of synthesis gas production and utilization begin to emerge: virtually any imaginable carbon source can be converted (at least in principle) to synthesis gas; coupling that process with a water gas shift reactor could in principle give hydrogen, *or* carbon monoxide, or a synthesis gas of any desired  $H_2/CO$  ratio. The tremendous versatility of hydrocarbon conversion, shift and synthesis is illustrated in the block flow diagram of Figure 20.8.

## Note

[A] Any time an extra step – such as the shift reaction – is added to a process, the capital cost and operating expenses are sure to increase. In rare instances it might be possible to offset the increased costs by selling by-products or through some enhancement that saves money elsewhere. Ideally it would be beneficial to avoid a shift reactor by having a process that provides a  $H_2/CO$  ratio in the product gas close to whatever value is needed downstream. In some cases there may even be economic benefit to accepting slight inefficiencies in either the feedstock conversion unit or the downstream synthesis process to avoid the additional expenses associated with a shift reactor. Nonetheless, the water gas shift is *the* key to adjusting the gas composition provided by the feedstock conversion to whatever value is required in the synthesis.

#### **Recommended reading**

Kohl, Arthur and Riesenfeld, Fred. *Gas Purification*. Gulf Publishing: Houston, 1985. An excellent, and extensive, resource on many techniques for gas clean-up, including acid gas removal, water removal, CO<sub>2</sub> absorption, and numerous others.

- Probstein, R.F. and Hicks, R.E. Synthetic Fuels. Dover: Mineola, NY, 2006. Chapters 3 and 5 of this very useful book relate to the present chapter. The Dover edition is a reprint of the earlier version published in the 1980s. Highly recommended to anyone working in this field. Rezaiyan, John and Cheremisinoff, Nicholas P. Gasification Technologies. Taylor and Francis:
- Boca Raton, 2005. Chapter 5, on gas clean-up technologies, is directly relevant to the material in this chapter.

# 21.1 Fuel gas

Hydrogen and carbon monoxide are readily combustible with high calorific values (–286 and –283 kJ/mol, respectively). Although the name synthesis gas reflects its intended use in subsequent operations for production of other fuels or chemicals, no technical issues prevent use of products of gasification (or partial oxidation or steam reforming) directly as fuels. Such products can be used for domestic heating and cooking, for process heat, or for raising steam in industry. Many countries had, at one time, significant infrastructure for making and distributing fuel gases from coal. Indeed, until the development of syntheses based on CO and H<sub>2</sub>, in the early decades of the last century, the whole purpose of converting coal to gas was for domestic or industrial heating and illumination. Current interest focuses on use of synthesis gas as fuel in IGCC plants.

Water gas, town gas, illuminating gas, and related fuels made from early coal conversion processes, as well as the products of oxygen-blown gasifiers, have calorific values in the range  $11-19 \text{ GJ/m}^3$ . Table 21.1 compares calorific values of some gases produced from coal with hydrogen, methane, and LPG.

A problem with some of these products is the high toxicity of carbon monoxide. Many gas-fired domestic appliances, such as water heaters or stoves, were equipped with pilot lights, in which a small quantity of gas was always being burned. Then, when the gas was turned on to the main burner or heater, it would be ignited by the pilot light, without a need to find matches. This bit of convenience for the householder, however, meant that if anything should cause the pilot light to go out, a small quantity of gas was now being emitted directly into the home. This offered the potential of slowly accumulating toxic, indeed lethal, concentrations of carbon monoxide. Especially in homes without carbon monoxide detectors, a gas leak could literally be fatal [A]. This problem gradually disappeared with the displacement of coal-derived gaseous fuels by natural gas in many countries. Nevertheless, carbon monoxide is still a killer, thanks to its presence in automobile exhaust and in the products of incomplete combustion in inefficient, poorly regulated wood or coal furnaces.

# 21.2 Methanation

For reasons discussed in Chapter 10, natural gas is a superb fuel. Its positive attributes are not shared by biomass, coal, or heavy oils. Worldwide, enormous investment exists in gas handling, storage, and distribution infrastructure, as well as electric plants,

Gaseous fuel	<b>Principal component</b> (s)	Calorific value, GJ/m <sup>3</sup>
Hydrogen	H <sub>2</sub>	12
Natural gas	CH <sub>4</sub>	38
LPG	$C_{3}H_{8}, C_{4}H_{10}$	104
Carbureted water gas	$H_2$ , CO, CH <sub>4</sub> , $C_2H_4$	20
Coke oven gas	$H_2, CH_4, N_2, CO$	22
Producer gas	$CO, H_2, N_2$	6
Town gas	$H_2, CH_4$	24
Water gas	$\tilde{CO}, H_2$	11

**Table 21.1** Comparison of calorific values of fuel gases made from coal with other common gaseous fuels. These data are intended for illustration; actual calorific values may vary, depending on the composition of the specific sample at hand. For gaseous mixtures, components are listed in decreasing order of concentration.

industrial heaters, domestic appliances, and vehicles fueled with gas. Coal and biomass are far more widely distributed around the world than is natural gas. Biomass can be a renewable fuel, with, in principle, no net carbon dioxide emissions. Projected lifetimes of remaining reserves of fossil fuels suggest that supplies of natural gas will be depleted long before coal [B]. Hence the potential exists for replacing current gaseous fuels with substitutes from coal and biomass gasification.

The process of methanation is the reverse of steam reforming of natural gas:

$$\text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}.$$

The product is known as substitute natural gas (SNG), or sometimes by the oxymoronic name synthetic natural gas. The largest plant for SNG production, in Beulah, North Dakota, uses lignite as feedstock, with FBDB gasifiers to make the synthesis gas.

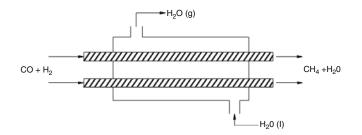
Upstream of methanation, the clean-up operations discussed in Chapter 20 are needed. Coupling methanation to gasification especially requires attention to the sulfur content of the feed to the methanation reactor, since the nickel catalysts commonly used are very susceptible to poisoning by sulfur. Sulfur concentration should be <1 ppm, ideally  $\approx 0.1$  ppm. This can be achieved by acid gas removal, possibly combined with a guard bed.

The ability to make methane from carbon monoxide and hydrogen, or vice versa, results from there being equilibrium among these species. Equilibrium constants always depend on temperature; in this case, low temperatures favor methanation. The equilibrium constant for methanation has a strong temperature dependence. Since methanation results in reduction of the number of moles of gaseous species, from four to two, high pressures favor methanation. Thus methanation reactors run at high pressures and low temperatures, while steam-reforming reactors operate at low pressures and high temperatures. Methanation is highly exothermic, not surprising since steam reforming reactions are endothermic (Chapter 19). Handling the excess reaction heat presents a challenge in design of methanation reactors.

Typical methanation processes operate at 260–370 °C and 1.5–7 MPa in the presence of nickel catalysts on alumina supports. Carbon monoxide chemisorbs onto the catalyst surface (Figure 21.1), accompanied by dissociative chemisorption of hydrogen, also



**Figure 21.1** Carbon monoxide chemisorbs on the catalyst surface, while hydrogen undergoes dissociative chemisorption to produce hydrogen atoms.



**Figure 21.2** A simple design for a methanation reactor, dealing with the significant exothermic heat of reaction, is a modification of a shell-and-tube heat exchanger (Figure 20.1). The catalyst is in the tubes, through which the synthesis gas is passed. Heat is absorbed by the water.

illustrated in Figure 21.1 The reaction proceeds as shown below in Figure 21.8, via a Langmuir–Hinshelwood mechanism.

The exothermicity of the reaction causes concern. Runaway reaction temperatures could sinter the catalyst, cause methane decomposition to carbon, or even result in explosion. In an uncooled adiabatic packed-bed reactor, probably the simplest reactor design that could be used, the heat of reaction causes the temperature to increase by  $60 \,^{\circ}\text{C}$  for every 1% of carbon monoxide converted to methane. Synthesis gas has high concentrations of carbon monoxide, so various methods must be used to keep the temperature from becoming unacceptably high. One is to run at low conversions and recycle gas to the reactor. Diluting the feed with recycled product allows adjusting the carbon monoxide concentration to increase the heat capacity of the feed gas, to help handle the expected heat release. Also, the recycled gas can be cooled before being injected back into the reactor. These tactics allow a reactor to run with a feed temperature of 300 °C and an outlet of 400 °C. Recovering the reaction heat presents an alternative approach. In almost any situation that provides a good deal of "free" heat, making steam almost always is a useful option. This could be done in methanation by using the tubes in a shell-and-tube heat exchanger as packed-bed catalytic reactors. Heat released by the reaction would be absorbed in water outside the tubes, see Figure 21.2.

Alternatively, a different reactor design could be used, e.g. a fluid-bed reactor instead of a packed or fixed-bed reactor. Though care must be taken to guard against sintering and coking of the catalyst, catalyst lifetimes of about five years are possible, with very high conversions. Fluidized-bed catalytic reactors, or entrained-flow designs, offer the advantage of having a high mass of catalyst relative to the feed gas. The catalyst absorbs much of the heat of reaction. In circulating fluidized bed or entrained flow reactors, the catalyst can be cooled by heat-exchange before being returned to the reactor. Catalyst sintering can be an issue in highly exothermic reactions such as methanation. The onset of sintering of nickel on a catalyst support might be expected around 590 °C. To avoid this problem, methanation reactors are run at  $\leq$ 525 °C, often well below this limit. It is also necessary to be on guard against formation of nickel carbonyl,

$$Ni + 4 CO \rightarrow Ni(CO)_4$$
,

a gaseous species that forms at low temperatures. Nickel carbonyl usually decomposes at  $\approx 150$  °C [C] but its formation and subsequent decomposition could result in a loss of nickel from the catalyst. Nickel carbonyl is also very poisonous, presenting a health and safety hazard.

For the water-gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

running in the direction shown to increase the  $H_2/CO$  ratio, the overall process could be simplified if the carbon dioxide did not have to be separated, but rather could be fed to the reactor as a reactant, not a diluent. The desired reaction would be

$$CO_2 + 4H_2O \rightarrow CH_4 + 2H_2O_2$$

Successful running of this reaction requires a catalyst capable of enhancing reactions of both carbon monoxide and carbon dioxide simultaneously. One such is a nickel-ruthenium alloy, on a support of lanthanum oxide.

An unusual application of methanation chemistry is in ammonia synthesis. Production of ammonia proceeds via the reaction

$$N_2 + 3 H_2 \rightarrow 2 NH_3.$$

Hydrogen can be produced via steam reforming of natural gas, followed by shifting to remove the carbon monoxide. However, the catalysts used in ammonia synthesis are readily poisoned by CO, so it is necessary to ensure that all CO has been removed upstream of the ammonia synthesis reactor. Removal of CO can be effected by methanation, producing a small amount of methane but, more importantly for this application, getting rid of a strong catalyst poison.

## 21.3 Methanol synthesis

Production of methanol from synthesis gas,

$$CO + 2H_2 \rightarrow CH_3OH$$
,

was discovered in 1913. Until the mid-twentieth century, the synthesis gas came from coal gasification. Since then, the preferred route to synthesis gas has been steam reforming using natural gas, LPG, or naphtha as feeds. Current methanol synthesis plants use natural gas as the source of the synthesis gas. Once the synthesis gas is available at the appropriate  $H_2/CO$  ratio, its source is not critical; in principle, future methanol plants could be based on gasification of biomass or coal, or partial oxidation of oil from oil sands. Making synthesis gas from biomass gasification would mean that, once again, methanol production would be biomass-based, but gasification followed by synthesis offers much higher yields of methanol per unit of biomass than would pyrolysis.

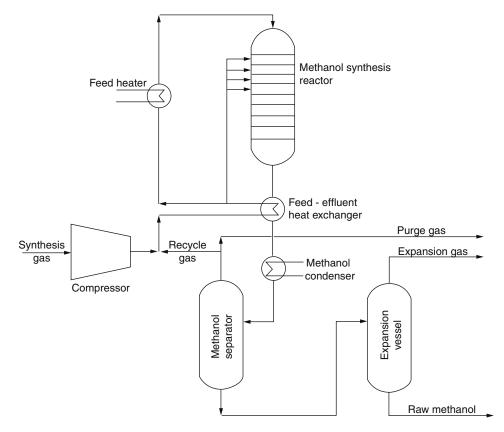
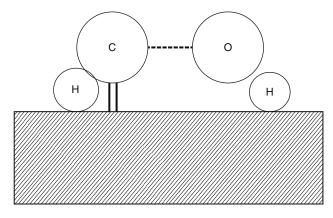


Figure 21.3 Process flow for a methanol synthesis operation, involving recycle of unreacted gas.

A flow diagram for methanol synthesis is given as Figure 21.3.

Similar to methanation, methanol synthesis is exothermic and occurs with a decrease in number of moles. Therefore, relatively low temperatures and high pressures favor driving the reaction to the right. Copper-based catalysts show good conversions at 260 °C and 5 MPa. Various strategies, similar to those used in methanation, maintain the temperature in the range of 250–270 °C. With a fixed-bed reactor, relatively cool feed gas can be injected at various parts of the reactor, or the feed is mixed with recycled gas. Alternatively, a reactor designed similarly to a shell-and-tube heat exchanger, as mentioned above, can be used.

Choice of catalyst is crucial, because of the potential for forming a wide variety of other liquid products from synthesis gas, via reactions to be discussed below. The catalyst must have a high selectivity for methanol. Formerly, typical process conditions were 400 °C and 30–38 MPa over zinc oxide catalysts, with a 62% conversion to methanol. The substantial reduction in severity obtained by use of the copper-based catalysts affords a significant improvement in economics. Copper catalysts are highly susceptible to poisoning by sulfur, so careful attention to upstream gas purification is needed. This would not be a problem if sweet natural gas or biomass were the precursor to the synthesis gas. Plants based on partial oxidation of heavy petroleum products or oil from oil sands, or on coal gasification, would certainly need H<sub>2</sub>S removal upstream of methanol synthesis.



**Figure 21.4** Reaction of chemisorbed carbon monoxide with hydrogen atoms forms an HCOH species on the catalyst surface.

A critical intermediate, HCOH, forms on the catalyst surface, shown in Figure 21.4. If the C–O bond breaks, the HC fragment will continue to add hydrogen, eventually forming methane. Alternatively, desorption and hydrogenation of the intact HCOH fragment leads to the desired methanol. Both zinc and copper are effective for hydrogenation of HCOH without C–O bond cleavage.

Steam reforming of natural gas, currently the preferred feedstock for methanol synthesis, produces a synthesis gas with  $H_2/CO$  of 3. This gas must be shifted to reduce the value to 2, the stoichiometric  $H_2/CO$  ratio required for methanol synthesis. To eliminate the need for a separate shift reactor,  $CO_2$  can be added with the feed to the steam reformer, such that three reactions occur simultaneously:

$$\begin{split} & CH_4 + H_2O \rightarrow CO + 3\,H_2, \\ & CH_4 + 2\,H_2O \rightarrow CO_2 + 4\,H_2, \\ & CO_2 + H_2 \rightarrow CO + H_2O. \end{split}$$

Methanol synthesis catalysts also convert carbon dioxide via the reaction

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O.$$

Because of this reaction, the presence of excess  $CO_2$  in the reactor is not a problem. If biomass or coal gasification were to be used as the synthesis gas source, this would not be an issue; in fact, the gas would have to be shifted to increase  $H_2/CO$ .

Methanol has numerous valuable uses in the chemical industry. The largest fraction goes to catalytic oxidation to formaldehyde,

$$2 \operatorname{CH}_3 \operatorname{OH} + \operatorname{O}_2 \rightarrow 2 \operatorname{H}_2 \operatorname{C} = \operatorname{O} + 2 \operatorname{H}_2 \operatorname{O},$$

used in production of phenol-formaldehyde resins and urea-formaldehyde foams [D]. Other products made from methanol include acetic acid, methyl *tert*-butyl ether (MTBE), and dimethyl ether. Dimethyl ether shows promise as a diesel fuel.

Methanol has a very high octane rating, and could be used as an octane-booster additive for gasoline. Unfortunately, several difficulties ensue. The most serious is the complete miscibility of methanol with water in any proportion. Small quantities of water added to a gasoline-methanol mixture cause the problem of "de-mixing," a total separation into two phases, a hydrocarbon phase and a water-alcohol phase [E]. Methanol forms azeotropes with some light hydrocarbons, such as hexane, thereby raising the vapor pressure and increasing the volatility of the blend. Methanol, even in small amounts, can change the elasticity, permeability and swelling behavior of polymers used to make fuel system components, such as hoses or seals.

There has also been interest in using mostly, or completely, pure methanol as a vehicle fuel. As with other alternative liquid fuels, interest in methanol seems to wax and wane with fluctuations in price and availability of petroleum. Pure methanol has a high heat of vaporization, 35 kJ/mol or 1100 kJ/kg. This makes it hard to create a good fuel-air mixture in the fuel intake system, and just about impossible to start a methanol-fueled vehicle at temperatures below  $0 \,^{\circ}$ C. Blending methanol with a liquid that is easier to vaporize circumvents this problem. Gasoline makes a good choice for the blending component, usually at 15%. An 85% methanol-15% gasoline blend is called M85. It is possible to design a vehicle to run specifically on M85. It could have a high compression ratio (possibly 12:1) to take advantage of the high octane rating, a fuel intake system designed around the vaporization problems, and methanol-compatible materials in the fuel system. It is likely that such a vehicle would give superb performance, but with the drawback of reduced fuel economy and driving range. Methanol has half the volumetric energy density of gasoline; for vehicles of similar design and weight driven under similar conditions, one could expect about half the fuel economy. If the fuel tank were of comparable size to those on gasoline-fueled vehicles, one would also experience about half the driving range before refueling. It is questionable whether there would be a deliberate effort to market vehicles specifically set up for operation on M85. The more promising alternative seems to be fuel-flexible vehicles (FFVs) that can run on fuels ranging from gasoline to M85 or E85.

Four points in favor of methanol merit its getting serious consideration as an alternative liquid fuel. First, it is a liquid. With appropriate attention to materials compatibility and to preventing water adulteration, methanol could be distributed via the same transportation, storage, and handling infrastructure as currently exists. Some other fuels that have their own technical merits – natural gas, for example – cannot make this claim. Second, because methanol can be produced from synthesis gas, in principle it could be made from any carbon-containing resource, including biomass, oil sands, municipal waste, and coal. Third, a very large manufacturing infrastructure already exists in many countries for production of methanol. In the event of a genuine or artificial shortage of petroleum, potentially methanol could be diverted from existing chemical markets to supply the transportation sector (albeit with significant dislocations in the chemical industry). Fourth, existence of methanol-to-gasoline technology (MTG, discussed in Chapter 14) can eliminate the concerns with using methanol or M85 as a fuel. The MTG product is not a liquid alternative to gasoline or compatible with gasoline; it *is* gasoline.

### 21.4 Fischer–Tropsch synthesis

The Fischer–Tropsch (F–T) synthesis was developed in Germany during the 1920s and 30s. Its name derives from its inventors, Franz Fischer [F] and Hans Tropsch [G].



**Figure 21.5** Frans Fischer, one of the great pioneers of synthesis gas chemistry.



**Figure 21.6** Hans Tropsch, who partnered with Fischer in development of the eponymous Fischer–Tropsch synthesis.

In early work, synthesis gas was reacted over a supported cobalt catalyst at  $\approx 200 \,^{\circ}\text{C}$ and 0.7–1 MPa, producing a complex mixture of hydrocarbons up to about  $C_{40}$ . The heavier compounds were useful as synthetic diesel fuel and synthetic lubricating oils. During World War II, some of the aviation and armored vehicle fuel used by the German military was produced via the F–T synthesis, with synthesis gas coming from coal gasification. This so-called medium-pressure synthesis provides products boiling in the gasoline, kerosene (jet fuel) and diesel fuel range, from  $C_3$  to about  $C_{18}$ . It represents a route to synthetic liquid fuels that could augment, or potentially replace, petroleum-derived fuels. American and British scientific teams investigating German wartime technology became enthusiastic about the remarkable potential for using coal to produce synthetic fuels and chemicals via the gasification-synthesis route. Further research was carried out by the United States Bureau of Mines using very inexpensive mill scale (a mixture of iron oxides and carbonates that forms on red-hot steel as it is processed in rolling mills) as catalyst. Reaction at 300-375 °C and 1.5-3.5 MPa produced a potentially useful synthetic gasoline with octane >70, and a variety of oxygenated compounds. However, it became clear that processes run in wartime conditions when economics was a secondary consideration could not compete with inexpensive, abundant petroleum in the postwar world.

The Fischer–Tropsch synthesis is the major application for synthesis gas made from coal, and thereby is the major route to making synthetic liquid fuels from coal. Conversion of solid coal to liquid transportation fuels via synthesis gas is known as indirect liquefaction. The adjective *indirect* indicates the existence of an intermediate processing step, i.e. converting coal to gas first, and then the gas to liquids. A simplified flow diagram showing how an indirect liquefaction plant would function is given in Figure 21.7.

Today the F–T synthesis so dominates the field of coal-to-liquids technology that many people seem to believe that "coal-to-liquids" *is* the F–T synthesis, which is certainly not true (e.g. Chapter 22). About 40% of the liquid fuels currently used in South Africa are made by indirect liquefaction from indigenous South African coals.

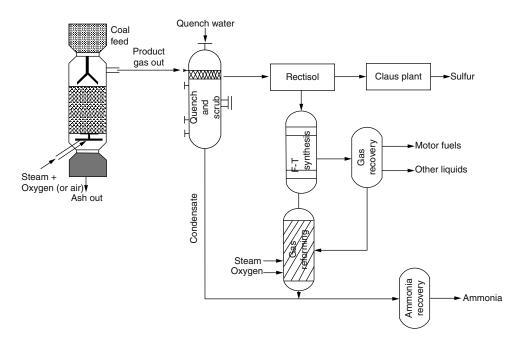


Figure 21.7 Process flow for an indirect coal liquefaction process, using fixed-bed gasifiers as the source of the synthesis gas.

Production of straight-chain alkanes in the F-T synthesis can be generalized as

$$(2n+1) H_2 + n CO \rightarrow C_n H_{(2n+2)} + n H_2O,$$

with a heat of reaction of -231 kJ/mol. Straight-chain alkenes are formed by

$$2n H_2 + n CO \rightarrow CnH_2n + n H_2O.$$

Reactions leading to alcohols are

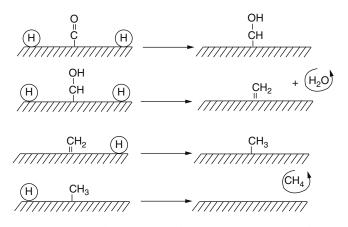
$$2n H_2 + n CO \rightarrow C_n H_{(2n+1)}OH + (n-1) H_2O$$

and

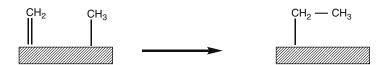
$$(n+1)$$
 H<sub>2</sub> +  $(2n-1)$  CO  $\rightarrow$  C<sub>n</sub>H<sub>(2n+1)</sub>OH +  $(n-1)$  CO<sub>2</sub>

In addition, some ketones, aldehydes or carboxylic acids may be produced. In some cases, the F–T reactions are accompanied by isomerization, dehydrocyclization, or both. In essence, almost any hydrocarbon product that could be derived from petroleum can be made from synthesis gas via the F–T reactions, given the appropriate choice of  $CO/H_2$  ratio, catalyst selectivity, and reaction conditions.

Metallic catalysts, especially Groups 8–10 of the periodic table, chemisorb both hydrogen and carbon monoxide. Events taking place on the catalyst surface have a key role in determining the product slate. In forming hydrocarbons, all the carbon monoxide in the feed must be destroyed, but in the formation of oxygenated products, at least one C–O bond must be preserved. The potential products range from  $C_1$  compounds, i.e. methane or methanol, to waxes in the  $C_{40}$  range. Since carbon monoxide contains only a single carbon atom, formation of products having two or more carbon atoms shows that oligomerization or polymerization must occur on the catalyst surface.



**Figure 21.8** A possible sequence of reactions ultimately leading to formation of methane from carbon monoxide and hydrogen. The process involves chemisorption of CO and dissociative chemisorption of  $H_2$ , formation of HCOH, loss of water and eventual formation of a methylene group, then a methyl group, and finally hydrogenation of the methyl to methane.



**Figure 21.9** An alternative to hydrogenation of a methyl group to produce methane is its reaction with a nearby methylene group. Effectively, the methylene group inserts into the bond between the methyl group and the catalyst surface. The result is an ethyl group on the catalyst.

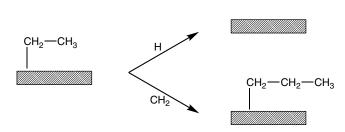
F–T hydrocarbon synthesis begins with dissociation of chemisorbed carbon monoxide, see Figure 21.8. The carbon atom bonded to the catalyst surface reacts with hydrogen atoms from dissociatively chemisorbed hydrogen to produce a methylene group; this in turn can react further to form a surface methyl group as shown in Figure 21.8. A potential outcome at this point is termination by reaction with an additional hydrogen atom to form methane, which desorbs from the catalyst surface. This sequence of steps represents methanation. To produce larger hydrocarbon molecules, it is necessary to account for the formation of carbon–carbon bonds on the catalyst.

In the Fischer–Tropsch process, the major change in the reaction mechanism, relative to methanation, is methylene insertion, see Figure 21.9.

At this point, the surface ethyl group can itself undergo termination to ethane, or further propagation by another methylene insertion to produce a surface propyl group. Figure 21.10 illustrates these processes.

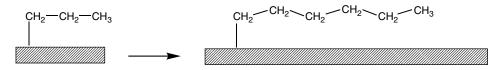
At each step, the options of termination or propagation by methylene insertion are available. Repetitive methylene insertions make it possible to build longer chains on the catalyst surface (Figure 21.11).

Products of five or more carbon atoms are liquid at ambient temperature. So, this sequence of methylene insertion reactions provides a route to synthetic liquid fuels from



**Figure 21.10** An ethyl group can become hydrogenated to ethane, which leaves the catalyst, or it can experience a second methylene insertion, to form a propyl group.

 $H_3C - CH_3$ 



**Figure 21.11** Multiple methylene insertions lead to formation of long hydrocarbon chains on the catalyst, as in this example of formation of a hexyl chain.

synthesis gas. The extent to which repetitive methylene insertion reactions occurs depends on reaction conditions, H<sub>2</sub>:CO ratio and choice of catalyst.

Changing the process variables modifies the reaction outcome with respect to the distribution of products that form. All of these modifications, though, seek the same objective, that of achieving a desired balance between chain growth on the catalyst surface and chain termination. In the Fischer–Tropsch, and related syntheses, the intent is to achieve a balance so as to produce liquid products. The same kind of balance between chain growth and termination is also important in polymerization, e.g. in making polyethylene. It can be described in terms of the Schulz–Flory distribution [H].

When a chain of carbon atoms grows on a catalyst surface, at any given step one of two events can occur: propagation or termination. The former adds one more carbon atom to the growing chain; the latter stops growth. Assuming that the probability of propagation vs. termination is constant regardless of chain length, then the amount of a compound having x carbon atoms will be some fraction of the amount of the compound having x-1 carbon atoms. The value of this fraction, given the symbol  $\alpha$ , is governed by the relative rates of propagation and termination, and can be found from

$$\alpha = r_{\rm p}/(r_{\rm p} + r_{\rm t})$$

where  $r_p$  is the rate of propagation and  $r_t$  of termination. Representing the weight fraction of the compound with x carbon atoms as  $M_x$ , then

$$\log\left(M_x/x\right) = c + x\log\alpha,$$

where *c* is a constant. A plot of log  $(M_x/x)$  as a function of *x* should be linear with slope of log  $\alpha$ . This relationship is the Schulz–Flory distribution. In practice,  $\alpha$  is often linear for values of  $x \ge 4$ . The relationship provides a way of predicting the distribution of

Increasing this	Causes this change in average molecular weight	
Pressure	increase	
Temperature	decrease	
$H_2/CO$ ratio	decrease	
Flow rate	decrease	

 Table 21.2 Summary of the effects of reaction variables in the Fischer–Tropsch process on the average molecular weight of the products.

various-sized molecules in the product. In most Fischer–Tropsch processes  $\alpha$  is usually 0.5–0.8. For the same conditions of temperature, pressure and catalyst,  $\alpha$  should be independent of the number of carbon atoms and the nature of the surface species on the catalyst. Therefore the product distribution can be described using  $\alpha$  as the only variable. The weight percent,  $W_x$ , of the product species containing *x* carbon atoms is given by

$$W_x = 100 x (1 - \alpha)^2 \alpha^{(x-1)}$$

As a rule,  $\alpha$  is directly proportional to pressure and inversely proportional to temperature. Using a supported ruthenium catalyst, at 0.1 MPa and 200 °C the principal product is methane, but at 100 MPa very high molecular weight products are formed. Generally, low values of  $\alpha$  and high temperatures produce lighter products; low temperatures and high  $\alpha$  values give lighter ones.

Formation of a distribution of products represents a potential disadvantage of the Fischer–Tropsch process. The maximum yield of gasoline ( $C_5-C_{10}$ ) occurs for  $\alpha$  of 0.76, but the yield is about 44%. Gasoline synthesis would be accompanied by a high yield of  $C_1-C_4$  gases. In practical operation the product distribution can be changed by changing operating conditions, the catalyst, or both. Regardless of what changes are made, the balance between propagation and termination gives a distribution of products. A consequence is the need for a sequence of separation and refining operations downstream of the F–T synthesis reactor. A major thrust of catalyst research is to find catalysts of better selectivity toward narrower ranges of products.

Increasing the  $H_2/CO$  ratio in the feed effectively increases the partial pressure of  $H_2$ . This increases the population of  $H_{\bullet}$  on the catalyst surface. Doing so increases the chances for termination relative to chain growth. In a medium-pressure synthesis, this enhances the yield of gasoline relative to diesel fuel. Increasing pressure favors adsorption and retards desorption. An increase in pressure should enhance chain growth at the expense of termination, and shift to higher molecular weight products. An increase in residence time allows more time for reactive species to stay on the catalyst. This also favors chain growth relative to termination. The product composition is shifted toward diesel. Increasing temperature helps to desorb species from the catalyst surface. This would shift the products toward the lighter end. Table 21.2 provides a summary of how reaction variables can be manipulated to change the product distribution.

The synthesis operates over a wide range of conditions, 150–350 °C and 0.5–4 MPa, depending on the required product distribution. Low temperatures favor formation of higher molecular compounds, while higher temperatures are used for gasoline production. Very high temperatures favor a high yield of methane. Catalysts are based on iron, cobalt,

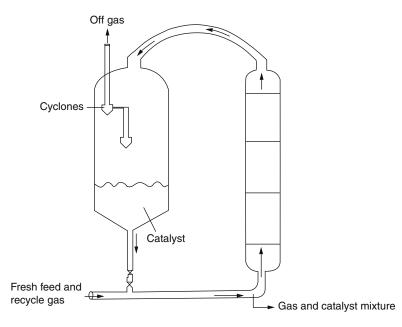


Figure 21.12 A circulating fluid bed catalytic reactor, for synthesis gas conversions.

or ruthenium. Usually cobalt catalysts are used with feed having  $H_2/CO$  in the range of 1.8 to about 2.1. Iron catalysts, however, promote the water gas shift reaction in the Fischer–Tropsch reactor, so tolerate lower  $H_2/CO$  ratios in the feed. As a rule, iron is not a highly active catalyst, but has the great virtue of being cheap. The catalyst is formulated with a potassium oxide promoter. Coke deposition on the catalyst is potentially a problem, but running with high concentrations of hydrogen in the feed gas reduces deposition.

Figure 21.12 provides a conceptual diagram of a circulating fluidized bed reactor for the F–T synthesis. Typical operating conditions would be 2.2 MPa and 310–330 °C. Practical operation must deal with the problem that the reaction is highly exothermic. Using water as a coolant provides a source of steam. In the catalyst hopper, the entrained catalyst particles disengage from the gas stream; most of the catalyst collects here. Cyclones remove any catalyst particles still entrained in the gas. The product is then washed in two steps, one with a recycle oil to dissolve relatively heavy hydrocarbons, and the other with water to condense light hydrocarbons.

Since the original work of Fischer and Tropsch in the 1920s, many variations of the basic process concept have been tested. Running at low temperature and high pressure shifts the product distribution toward higher molecular weights. A substantial increase in pressure relative to medium-pressure synthesis reduces the likelihood of molecules desorbing from the catalyst surface. Considering the adsorption/desorption process as an equilibrium:

#### $A(ads) \rightleftharpoons A(gas),$

Le Chatelier's Principle indicates that increased pressure will shift the equilibrium to the left. The high-pressure synthesis operates at 100–150 °C but pressures up to 100 MPa. Reducing temperature means that less thermal energy is available to help molecules desorb. Both changes therefore favor a longer lifetime for adsorbed

species on the catalyst surface, and methylene insertion reactions are favored at the expense of desorbing relatively small molecules. The catalyst is ruthenium on an alumina support. The main product is wax, with melting points up to  $\approx 135$  °C. Reducing the  $CO/H_2$  ratio in the feed encourages formation of lower molecular weight compounds. If the value is reduced all the way to 0.25, then about 96% of the product is methane. The iso synthesis uses thorium oxide (thoria) or thoria-alumina catalyst at 400-500 °C and 10-100 MPa. Potassium carbonate is used as a promoter. Major products are  $C_4$  and  $C_5$  branched-chain alkanes, about 75% being 2-methylpropane (isobutane). Short branched-chain hydrocarbons, e.g.  $C_4$  and  $C_5$ , can be converted to synthetic rubber. Oxide catalysts can effect structural rearrangements in hydrocarbon chains by directing the reaction through carbocation intermediates, resulting in an increased octane number of the gasoline fraction produced. Temperatures above 400 °C encourage production of aromatics along with the branched-chain alkanes; below 400 °C, production of oxygenated compounds also occurs. The synthol synthesis produces straight-chain alcohols at 400–450 °C and 14 MPa over an iron catalyst.

The value of Fischer–Tropsch waxes is that they can be selectively hydrocracked into diesel fuel and naphtha. The resulting fuel products are exceptionally clean, of zero sulfur content. The diesel fuel has a very high cetane value. These two characteristics make Fischer–Tropsch diesel a very desirable fuel. An additional value of making waxes comes from being able to "unzip" the wax molecules in a series of  $\beta$ -bond scission reactions to produce high yields of ethylene, e.g.

$$\begin{split} \mathbf{R}-\mathbf{C}\mathbf{H}_2-\mathbf{C}\mathbf{H}_2-\mathbf{R}' &\rightarrow \mathbf{R}-\mathbf{C}\mathbf{H}_2\bullet + \bullet\mathbf{C}\mathbf{H}_2-\mathbf{R}', \\ \mathbf{R}-\mathbf{C}\mathbf{H}_2\bullet &\rightarrow \mathbf{R}''-\mathbf{C}\mathbf{H}_2\bullet + \mathbf{C}\mathbf{H}_2=\mathbf{C}\mathbf{H}_2. \end{split}$$

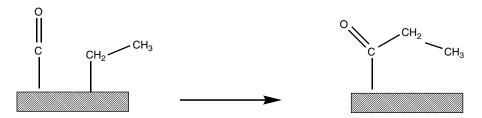
Ethylene represents the starting point for large-scale production of such commodity plastics as polyethylene, poly(vinyl chloride), and poly(ethylene terephthalate). Wax unzipping involves forming a large volume of gas by repetitive endothermic bondbreaking reactions. Low-pressure, high-temperature conditions favor unzipping. Running the thermal cracking of waxes at lower temperature provides less thermal energy for endothermic bond scission reactions, and running at higher pressure favors more collisions that could enhance, among others, hydrogen abstraction reactions. A possible sequence of reactions leads not to ethylene but to longer-chain 1-alkenes, e.g.

$$\begin{aligned} \mathbf{R}'-\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{2}-\mathbf{R}''+\mathbf{R}\bullet &\rightarrow \mathbf{R}'-\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}\bullet-\mathbf{R}''+\mathbf{R}\mathbf{H},\\ \mathbf{R}'-\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}\bullet-\mathbf{R}'' &\rightarrow \mathbf{R}'-\mathbf{C}\mathbf{H}_{2}\bullet +\mathbf{C}\mathbf{H}_{2}=\mathbf{C}\mathbf{H}-\mathbf{R}''. \end{aligned}$$

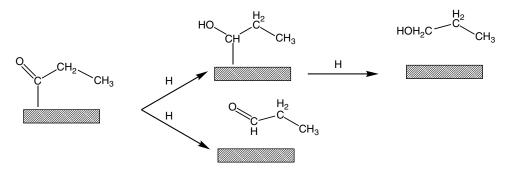
Known in industrial practice as  $\alpha$ -olefins, 1-alkenes are valuable chemical feedstocks in their own right for making, as examples, detergents, plasticizers, and alcohols.

Running the F–T reaction with a very low  $H_2/CO$  ratio leads to high populations of species as shown in Figure 21.8 on the catalyst surface. Formation of oxygenated compounds requires a carbon monoxide insertion (Figure 21.13). Then, formation of an alcohol occurs by subsequent reaction with hydrogen atoms (Figure 21.14).

Formation of longer-chain alcohols is analogous. Aldehyde by-products form, also shown in Figure 21.14. These compounds have commercial uses as intermediates to other chemical products or as solvents. Aldehydes with three to eight carbon atoms are used, for example, to produce such compounds as ethyl acetate. These aldehydes



**Figure 21.13** At low  $H_2/CO$  ratios, chemisorbed carbon monoxide can insert into the bond between the growing hydrocarbon chain and the catalyst, adding a carbonyl group to the molecule being formed.



**Figure 21.14** Subsequent reaction after the carbonyl insertion of Figure 21.13 can lead either to aldehyde formation or to alcohol formation.

tend to have obnoxious odors; for example, a major contribution to the smell of rancid butter comes from butanal (butyraldehyde). In contrast, long-chain aldehydes, of about nine to fifteen carbon atoms, have very pleasant fragrances. Their applications include use in detergents and other household products to create a so-called "lemony" scent.

# 21.5 Kölbel reaction

The Kölbel reaction [I] can be thought of as a variation of the F–T synthesis in which the product being rejected is carbon dioxide rather than water. Thus

$$2n \operatorname{CO} + n \operatorname{H}_2 \rightarrow (-\operatorname{CH}_2)_n + n \operatorname{CO}_2,$$

for which the heat of reaction is -228 kJ/mol. The Kölbel process makes use of a slurry column reactor. In this device, synthesis gas flows upward. The reactor is packed with an iron catalyst suspended in a heavy liquid or wax. The reactor operates at  $\approx 1.2 \text{ MPa}$  and 260–280 °C. Because the rejected material, CO<sub>2</sub>, contains carbon rather than hydrogen, the Kölbel reaction makes it possible to produce hydrocarbons using a lower H<sub>2</sub>/CO ratio in the feed than would be used in the F–T synthesis, as low as  $\approx 0.67$ . The Kölbel reaction offers the possibility of eliminating the water gas shift to reduce the

 $CO/H_2$  ratio. A variant is the Kölbel–Engelhard reaction, which uses a mixture of carbon monoxide and water as the feed:

$$3n \operatorname{CO} + n \operatorname{H}_2 \operatorname{O} \rightarrow (-\operatorname{CH}_2)_n + 2n \operatorname{CO}_2.$$

This is equivalent to running with a  $H_2/CO$  ratio of 0.

The Kölbel reaction has two disadvantages, relating to the rejection of CO<sub>2</sub>. First, the reaction wastes some of the carbon from the feed used to make the synthesis gas, since necessarily some carbon exits as  $CO_2$  and not in the desired hydrocarbon products. Second, rejecting  $CO_2$  adds to the total  $CO_2$  emission from the plant, or would require a larger  $CO_2$  capture operation in the plant. Neither option is desirable from the standpoint of process economics or environmental issues.

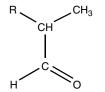
# 21.6 Oxo synthesis

The Oxo process was developed in Germany during the 1930s as a route to synthesis of alcohols. The original interest was for synthesis of  $C_{12}$ – $C_{18}$  alcohols, which could be converted subsequently to sulfate esters used in detergents [J]. The Oxo process is an important industrial route to aldehydes, precursors to alcohols. In addition to use in making detergents, some of these alcohols, particularly the shorter-chain alcohols, react with phthalic acid to form phthalate esters, used as plasticizers.

The Oxo process involves hydroformylation reactions, e.g.

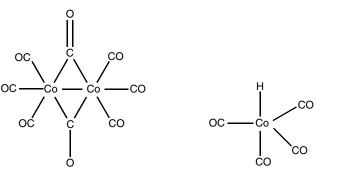
$$R-CH = CH_2 + CO + H_2 \rightarrow R-CH_2CH_2CHO.$$

This reaction adds one carbon atom to the chain. Addition across the double bond is not specific, so branched aldehydes are also formed, e.g. 21.1.



21.1 A branched aldehyde

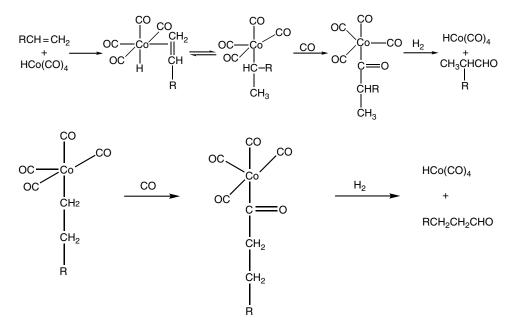
The Oxo process employs dicobalt octacarbonyl, Co<sub>2</sub>(CO)<sub>8</sub>, (21.2) as catalyst.



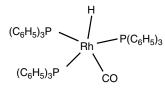
21.2 Dicobalt octacarbonyl

21.3 The catalytically active species

The actual catalytically active species in the reaction may be  $HCo(CO)_4$  (21.3). The reaction occurs in the liquid phase, with the cobalt species probably functioning as a homogeneous catalyst. What probably happens is along with



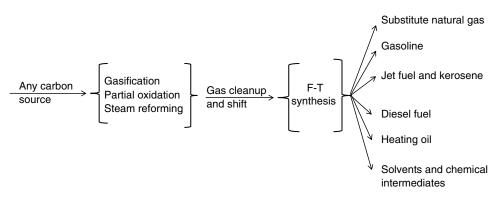
In these reactions, the alkene coordinates with the cobalt atom, forming a bond between the cobalt atom and an alkyl carbon atom. This bond can form with either of the two carbon atoms originally involved in the alkene double bond. Carbonyl insertion with carbon monoxide adds the aldehyde carbonyl group; reaction with hydrogen then generates the free aldehyde product and regenerates the catalyst. New catalyst formulations involving rhodium as the active metal, with phosphines or other ligands, have been developed, such as  $Rh(Ar_3P)3(H)$  (CO) (21.4).



21.4 New catalyst formulations have involved rhodium

# 21.7 Gas to liquids

Though much of the foregoing discussion has presumed that coal or biomass gasification would be the source of the synthesis gas, using natural gas provides an alternative. Steam reforming of natural gas, followed by one of the processes discussed above, also offers a route to synthetic liquid fuels. The overriding principle has been mentioned previously: once synthesis gas has been produced, cleaned and shifted, the original feedstock used to make the gas becomes irrelevant.



**Figure 21.15** Starting with any carbonaceous material and converting it to synthesis gas of the appropriate  $H_2/CO$  ratio, it is then possible to select a catalyst and reaction conditions to produce the entire spectrum of hydrocarbon fuel products plus an array of useful chemicals and polymers.

Gas-to-liquids (GTL) technology merits serious consideration as a route to liquid transportation fuels. A large plant in Malaysia currently produces middle distillate fuels from natural gas, utilizing a variant of the Shell gasification process for steam reforming. Another plant is coming on line in Qatar. This raises the question of why energy and effort should be expended to convert a very good quality fuel, natural gas, into a different fuel form. First, natural gas distribution via pipeline is well-established technology, but cannot be used for trans-oceanic shipping of gas. Natural gas can be transported on ships as compressed gas or liquefied gas (LNG). Both approaches work, but neither is ideal. Because a catastrophe could occur from an explosion of an LNG tanker in the harbor of a major metropolitan area, some countries now require that LNG unloading facilities be placed a long distance off shore, with the gas flowing by pipeline to on-shore handling and distribution centers. A second reason for considering GTL technology would be in countries or regions with abundant indigenous gas resources but little petroleum. GTL provides a way to satisfy demand for liquid fuels without relying so heavily on imports. This situation motivated construction of the MTG plant in New Zealand, where the intent was to utilize offshore deposits of natural gas to manufacture gasoline. Much interest is now focused on development of shale gas resources in the United States. If the optimistic predictions about the size of the resource are correct, this gas could be an immense source of energy for decades. The U.S. has been importing more petroleum than is produced domestically since the 1970s. It remains to be seen whether the shale gas deposits will be coupled with GTL plants.

## 21.8 The potential of synthesis gas chemistry

The block-flow diagram of Figure 21.15 indicates how synthesis gas production and use can be put together on a large scale.

The tremendous versatility obtained by combining the carbon-steam reaction, the water gas shift, and the Fischer-Tropsch (and related) syntheses cannot be

overemphasized. Feedstocks could include natural gas, petroleum fractions or resids, coal, biomass, oil sands, oil shale, or municipal wastes. Multiple feedstocks could be accommodated either in parallel process trains or by co-feeding, such as feeding mixtures of coal and biomass to gasifiers. Potential products include substitute natural gas, methanol, gasoline, aviation fuel, diesel fuel, fuel oils, ethylene (for conversion to plastics),  $\alpha$ -olefins (for conversion to various chemicals), and hydrogen. In other words, all of the fuel products and a great many of the chemical products now in use worldwide could be supplied from synthesis gas, which in turn could be made from almost any carbon source. The synthesis gas technology could be selected depending on local resource availability. For example, if natural gas is abundant, steam reforming makes sense; for somewhere else, perhaps biomass gasification or oil sand partial oxidation would make better use of available resources. Furthermore, the synthesis gas production processes could evolve with time. As an example, one scenario might find it desirable to build and operate a plant based on steam reforming of natural gas, but if gas supplies dwindle over the years, the plant could then be retrofitted with gasifiers and gas clean-up operations.

#### Notes

- [A] One reason why carbon monoxide is so insidious a killer is that, in early stages of CO poisoning, it causes drowsiness. A family that had retired for the night could fall into an even deeper sleep as CO slowly filled the house, and never wake up. Because the combustion stoichiometries of water gas and natural gas are different, efficient combustion requires slightly different burner tips or nozzles for each fuel. I grew up in a home having domestic appliances that used water gas made from anthracite. When natural gas became available in our town, a technician from the gas company came to the house to change the burner tips in the stove. He assured us that, with natural gas, we need never fear accidental carbon monoxide poisoning again. Apparently mindful of the fact that methane forms explosive mixtures with air, he quickly added that, with natural gas, we now faced the prospect of blowing ourselves up.
- [B] A potentially major revolution in the energy economy, currently taking place in several countries, is the exploitation of shale gas, sometimes called tight gas. If the resource estimates are reasonably accurate, and if this gas can be recovered without damage to the environment, its availability in vast quantities could substantially change thinking in a number of areas, for example downplaying substitute natural gas while shifting much more focus onto gas-to-liquid technology.
- [C] Formation and subsequent decomposition of nickel tetracarbonyl is the basis of the Mond process for purifying nickel. Nickel reacts with carbon monoxide at temperatures as low as 60 °C. The gaseous tetracarbonyl migrates away, leaving any impurities behind. Then, at ≈230 °C, nickel tetracarbonyl decomposes back to nickel (now pure nickel) and carbon monoxide. This process can be used not only to produce particles of pure nickel, but also to nickel plate metal surfaces or produce nickel mirrors.
- [D] The most important use of phenol-formaldehyde resins nowadays is in production of circuit boards. The first such material to be commercially produced on a large

scale was Bakelite, developed about a century ago. It quickly found a myriad of uses, ranging from billiard balls to fountain pens to jewelry. Originally intended as a very cheap substitute for wood or metal articles, Bakelite items from the early twentieth century are now collector's items. Urea-formaldehyde foams once had widespread application as home insulation, but such use was discontinued in some countries due to concerns about formaldehyde emissions into the home. Ureaformaldehyde has wide use as a fertilizer, for controlled release of ammonia and carbon dioxide into the soil. The resins continue to find use in adhesives and various plastic household items.

- [E] Aside from the genuine technical problems associated with demixing, this phenomenon also brings with it an unfortunate choice of terminology. When demixing occurs in a gasoline-methanol-water system, the separation of the second phase can give the liquid a milky or cloudy appearance. The point at which enough water has been added to cause demixing is sometimes called the cloud point. The cloud point associated with phase demixing is *not* the same thing as the cloud point caused by wax precipitation at low temperatures.
- [F] Franz Fischer (1877–1947) developed the process that bears his name during the 1920s. In addition to his many contributions to research, Fischer was also the first director of the Max Planck Institute for Coal Research in Mulheim, Germany (originally called the Kaiser Wilhelm Institute for Coal Research).
- [G] Hans Tropsch (1889–1935) worked with Fischer at the Kaiser Wilhelm Institute for Coal Research, but later left to take up a professorial position in the Institute for Coal Research in Prague. He also spent some time in the United States, including at Universal Oil Products, now known as UOP.
- [H] Also known as the Anderson–Schulz–Flory distribution, in part for the American chemist Paul Flory (1910–1985; Nobel Prize, 1974), who was one of the leading polymer scientists of the twentieth century. Flory's best-known book, *Principles of Polymer Chemistry* (Cornell University Press, 1953), remains a very useful resource nearly sixty years after its original publication.
- [I] Named in honor of Professor Herbert Kölbel (1908–1995), who served as director of the Institute of Technical Chemistry at the Technical University of Berlin. Kölbel was a prolific author of journal articles and patents in the field of synthesis gas chemistry for many decades during the mid-twentieth century.
- [J] The sulfate esters of long-chain aliphatic alcohols are known in the detergent industry as linear alcohol sulfates (AS). They are particularly noteworthy for producing a good foam. Though other kinds of compound, notably the linear alkylbenzenesulfonates (LAS) have a larger market share, the good foaming characteristics of the AS compounds makes them desirable components of shampoos.

#### **Recommended reading**

- Berkowitz, N. *An Introduction to Coal Technology*. Academic Press: New York, 1979. Chapter 12 of this fine book contains material relevant to synthesis gas conversion.
- Guibet, J.C. *Fuels and Engines*. Éditions Technip: Paris, 1999. A very thorough two-volume work covering the traditional petroleum-derived fuels and many alternative fuels, as well as information on engine performance and exhaust emissions. Chapter 6 includes a discussion on methanol and M85.

- Higman, Christopher and van der Burgt, Maarten. Gasification. Gulf Professional Publishing: Burlington, MA, 2008. An excellent book on gasification technology. Chapter 7 provides a very useful discussion of applications of synthesis gas in production of fuels and chemicals.
- Lee, Sunggyu. *Alternative Fuels*. Taylor and Francis: Washington, 1996. Chapter 3 discusses gasification and the uses of synthesis gas for production of fuels and chemicals.
- Probstein, R.F. and Hicks, R.E. Synthetic Fuels. Dover Publications: Mineola, NY, 2006. A thorough discussion of fundamentals and practical aspects of synthetic fuel technology. Chapters 3, 5, and 6 contain useful information pertinent to the present chapter.
- Schobert, Harold H. *The Chemistry of Hydrocarbon Fuels*. Butterworths: London, 1990. Chapter 12 discusses some of the historical approaches to coal gasification and its products; and processes that were important in the development of technology but are now largely obsolete.
- Speight, James G. *Synthetic Fuels Handbook*. McGraw-Hill: New York, 2008. This book reviews production of synthetic fuels from a wide range of feedstocks, including fossil and biofuels, and wastes. Chapter 7 treats the production of fuels from synthesis gas.

# 22 Direct production of liquid fuels from coal

Coal occurs in immense quantities in many countries. The estimated lifetime of coal reserves substantially exceeds those of natural gas and petroleum. Prospects for commercializing biofuels increase continuously, but it remains a question whether it will be possible to grow enough biomass to meet liquid fuel market demands, particularly without impacting food production. At the same time, an immense investment has been made worldwide in vehicles, airplanes, ships, and stationary combustion sources that use liquid fuels. Replacing this infrastructure with alternatives using solid or gaseous fuels or electricity would require many decades. A need for liquid fuels will continue throughout the foreseeable future. For these reasons, technologies for producing liquid fuels from coal merit serious attention.

Gasification followed by Fischer–Tropsch synthesis represents the currently dominant coal-to-liquids technology. However, many other processes are available to produce useful liquid fuels from coal. In its broadest sense, the term *liquefaction* refers to a conversion of something (usually a solid) into a liquid. Aside from the indirect liquefaction discussed in Chapter 21, liquids can be produced from coal by thermal breakdown of the coal structure (pyrolysis), by dissolution of coal components (solvent extraction), or by reaction of coal with hydrogen or with solvents capable of donating hydrogen (hydroliquefaction). All four approaches, i.e. including F–T, constitute the field of coal-to-liquids (CTL) technology. Although the word liquefaction could embrace any of these, as customarily used it refers to F–T synthesis or hydroliquefaction.

# 22.1 Pyrolysis

Pyrolysis of biomass, heavy petroleum fractions, oil sands, oil shale, and coal usually produces some amount of liquid product. Pyrolysis conducted without an externally added source of hydrogen is constrained by the amount of hydrogen originally available in the feedstock, i.e. by the inevitable requirement that formation of hydrogen-rich, high H/C products must be accompanied by formation of carbon-rich, low H/C products. Pyrolysis produces liquids, but leaves a residue of carbonaceous char or coke. Usually the process cannot be controlled so precisely as to obtain only liquids as the hydrogen-rich products; gases also form. The relative proportions of solid, liquid, and gas depend on the nature of the feedstock and on the range  $20\pm10\%$ . So, while pyrolysis produces liquids, and represents the simplest process for doing so, unless markets or internal uses exist for the solid and gaseous products, pyrolysis is

very wasteful, uneconomic, and, in many parts of the world, will sooner or later draw the unpleasant attention of environmental regulatory agencies.

Selection of a specific feedstock has a significant role in determining the product slate and product quality, because that selection fixes the H/C ratio of the feed. The total yield of liquid plus gaseous products increases with increasing H/C ratio. The outcome also depends on the usual reaction variables, temperature, pressure, and residence time, and often on particle size of the feed as well. Generally, high pressures reduce the yields of light liquid products, and lower pressures enhance yields. If the high pressure keeps the products in the reactor longer, more extensive cracking to gases is likely. Particle size affects the internal heating of the particle. Relatively large particles might not be heated uniformly all the way through during their residence time in the reactor; consequently pyrolysis yields are less. Heating rate is also important. During slow heat-up, as might be expected in simple equipment such as kilns, most coals begin to decompose in the temperature region around 350–400 °C. Production of liquid and gaseous products hits a peak usually between 425 and 475 °C. This phase of pyrolysis ends around 500 to 550 °C. In comparison, very rapid heating, in entrained-flow gasifiers for example, quickly by-passes this stage, so that evolution of pyrolysis liquids is nil.

Temperature is significant in determining the liquid composition. Low-temperature tars, produced at temperatures <700 °C, contain a wide variety of alkylaromatics, alkanes and alkenes, alkylphenols, and alkylpyridines. In comparison, high-temperature tars, made at temperatures well above 700 °C, consist mainly of polycyclic aromatics from which the alkyl side chains have been removed completely or reduced to methyl groups, phenols, and polycyclic nitrogen-containing heterocycles, e.g. quinolines. High-temperature tars are by-products of metallurgical coke manufacturing (Chapter 23).

The composition of liquids reflects both the chemical nature of the feedstock and the reaction conditions. Most of the carbon in most coals is in aromatic structures. Coals contain usually 1-2% nitrogen, 1-5% sulfur, and 2-25% oxygen. Some of these heteroatoms are incorporated in relatively refractory structures in the coal, such as benzoquinoline or dibenzothiophene. Even allowing for variations due to the specific coal pyrolyzed and the effect of specific reaction conditions, it can be expected that the pyrolysis liquids are highly aromatic; contain some nitrogen, sulfur, and oxygen; and have a high viscosity. About the only virtue is that the mineral matter has been left behind in the char or coke.

Coal pyrolysis is made complicated, both in the laboratory and in practical processes, by the fact that the products initially released from the thermal breakdown of the coal structure – primary pyrolysis products – are themselves reactive organic compounds still experiencing high temperature, and are able to react among themselves, to react with steam (from the moisture in the coal), to react with the char or coke, or to do several of these things at once. The products actually collected and analyzed – often called secondary pyrolysis products – may differ in structure or composition from the primary products initially released. Primary products can be collected and studied in the laboratory if provision is made either to quench them rapidly as they form, or to feed them directly into a suitable analytical instrument, such as a gas chromatograph. In industrial practice the design of the pyrolysis reactor affects the composition of the liquid products, because reactor design determines how long the primary products are exposed to pyrolysis temperatures, establishing the likelihood of secondary reactions. Commercially, the main applications of pyrolysis have been to produce either a useful gaseous fuel (e.g. town gas) or to produce a char for various applications [A]. Liquids as produced directly from pyrolysis are unsuitable for immediate use as fuels in stationary combustion equipment or engines. Some sequence of downstream operations would be required to obtain liquids of suitable technical quality and environmental standards to be marketed and used. Nonetheless, low-temperature tars can be refined successfully into gasoline or diesel fuel. Treating raw tar with aqueous sodium hydroxide removes phenols. Then, an appropriate combination of hydrotreating to reduce sulfur and nitrogen contents, hydrogenation to saturate aromatic compounds, and hydrocracking to open cycloalkane rings or to reduce the size of alkanes, provides clean liquid fuels. Catalysts and reaction conditions are generally similar to those used in refining middle distillates (Chapter 15).

The technical details and the economic driving forces for a commercial coal pyrolysis process depend on the principal product(s) required for local markets. A process could be established with the primary goal of making town gas, taking (or accepting) liquids and char as by-products. Alternatively, the process could make, as the main product, a char or coke for the metallurgical industry or for domestic use as a smokeless fuel, with gases and liquids as by-products. Yet another alternative would focus on liquids production. Prior to World War II most commercial low-temperature technology was aimed at making solid fuels. They became unattractive with the widespread availability of cheap oil in the 1950s. Then, with the oil embargo and oil price shock of the 1970s, interest was revived, but with the notion of using pyrolysis to make gaseous or liquid fuels. With a decline of world oil prices in the 1990s, interest faded again. Possibly, future events on the world energy scene will revive interest once more. Pyrolysis offers relative simplicity of process and equipment design relative to gasification and hydroliquefaction. On the other hand, competing technologies usually provide high yields of a single type of product (i.e. gas, liquid, or solid), an advantage which may offset the added complexity and cost of process.

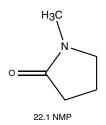
The rules change when an external supply of hydrogen is made available. Hydropyrolysis, i.e. pyrolyzing coal in a hydrogen atmosphere, increases the yields of liquids and gases relative to inert-atmosphere pyrolysis. The hydrogen atmosphere stabilizes radicals by hydrogen capping before they are able to experience termination by recombination reactions that would lead to char formation. Despite this advantage relative to more conventional pyrolysis, hydropyrolysis has never been commercialized.

# 22.2 Solvent extraction

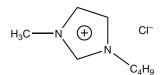
As applied to production of liquids from coal, the term solvent extraction has several meanings. It could represent treatment of coal with a solvent to dissolve some components of the coal. This process may involve some chemical reaction, but not extensively. The solvent could be stripped off to recover the extract, or the mixture of solvent and extract might be processed together. If the extract is intended to be used as a fuel, one or more downstream refining steps will be needed to produce acceptable specification-grade products. Alternatively, the term could also represent treating coal with a reactive solvent, usually hydroaromatic compounds that are able to transfer hydrogen to the molecular fragments being liberated from the coal. This latter strategy is also called

donor-solvent liquefaction, and is discussed later, in the section on direct liquefaction processes. When temperatures are such that the coal is undergoing thermal decomposition, the distinction between solvent extraction and direct liquefaction becomes rather arbitrary.

Solvent extraction has been used for over a century as an approach to studying the composition of coal in the laboratory. Most solvents used in this application fall into one of two categories. Many common solvents used in an organic chemistry laboratory – chloroform, acetone, benzene, or diethyl ether as examples – usually dissolve only a few percent ( $\leq 10\%$ ) of the coal. Most of what does go into solution comes from plant waxes or resins that survived coalification and remain in the coal. A second set of solvents, including pyridine, quinoline and 1,2-diaminoethane (ethylene diamine), can dissolve up to  $\approx 40\%$  of a coal, apparently without involving breaking of bonds. Most of the solvents that perform in this way have in their molecules at least one nitrogen or oxygen atom with unshared pair(s) of electrons. Solvent pairs sometimes extract far more material than either solvent does alone. The best such combination is a mixture of carbon disulfide and *N*-methylpyrrolidone (NMP (22.1)).



With any solvent, extract yields vary from one coal to another, but in favorable cases, a CS<sub>2</sub>-NMP mixture is capable of dissolving up to  $\approx 80\%$  of some bituminous coals. Ionic liquids, e.g. butylmethylimidazolium chloride (22.2), may be able to extract even higher percentages, at temperatures  $\leq 100$  °C.



22.2 Butylmethylimidazolium chloride

At 300 °C and above, compounds such as phenol, 2-naphthol, anthracene, and phenanthrene are effective solvents. This temperature range also marks the onset of active thermal decomposition of most coals, so it becomes a semantic issue whether the solvent is dissolving the coal itself, is solubilizing molecular fragments produced by the thermally induced breakdown of the coal structure, or is chemically participating in decomposing the coal structure (the process of solvolysis).

Different solvents produce different extract yields from the same coal. As a rule, the yield produced by the same solvent from different coals decreases with increasing rank,

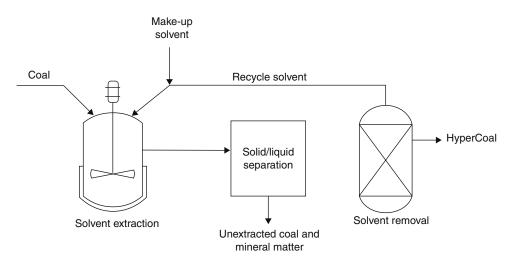


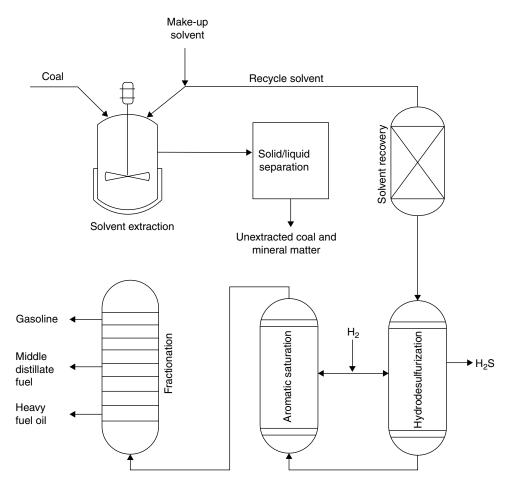
Figure 22.1 Process flow for the HyperCoal process, producing a solid fuel of near-zero ash value.

at least in the subbituminous and bituminous rank ranges. Vitrinites and exinites represent the most extractable portions of the coal, whereas intertinites tend to dissolve to a much lesser extent. Anthracites give very low yields, <5%, regardless of the solvent used. Yield from the same coal:solvent combination increases with increasing temperature, and increases with decreasing particle size of the coal.

With the good solvents such as pyridine and quinoline, and with solvent pairs, the extract has nearly the same elemental composition and spectroscopic properties as the original coal. This raises the question of whether the "extracts" are really true solutions, or are mostly colloidal dispersions of micro- or nanosized particles of the coal. For some industrial processing by solvent extraction, such as the HyperCoal process discussed below, the distinction may not be of practical importance.

The Pott–Broche process, developed in Germany in the 1930s, extracts coal with a mixture of tetralin and cresol in 4:1 ratio. Temperature, pressure, and residence time were 415–430 °C, 10–15 MPa, and 1 hour, respectively. Yields were in the order of 80%. The primary liquid was hydrogenated to produce gasoline and diesel fuel. The Ude–Pfirrmann process employed a hydrogen atmosphere, higher pressures ( $\approx$ 30 MPa) and shorter residence times (30 min.). Probably because of the additional hydrogen in the extraction step, the Ude–Pfirrmann product had a higher hydrogen content and lower heteroatom content, and was used directly as a fuel for stationary diesel engines.

Combustion turbines find application in IGCC plants, fired with synthesis gas, and in installations generating peak-load electricity, usually fired with natural gas. If these units could be fired with coal, the gasification and gas clean-up steps could be eliminated from an IGCC plant. Where coal is used in base-load electricity generation, it could also be applied in a nearby peak-load plant. The stumbling block is mainly the mineral matter in coal. Particles of ash could erode turbine blades, stick to blades and corrode them, or, by sticking in different amounts on different blades, could unbalance the turbine. In any of these cases, catastrophic failure of the turbine could result. The HyperCoal process was developed to produce an essentially ash-free coal (nominally <0.02% ash value) that could then be used as a fuel for turbines.



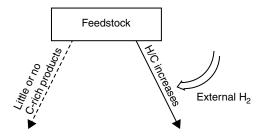
**Figure 22.2** Process flow for a solvent extraction process developed at Penn State University for production of clean middle-distillate fuels.

The HyperCoal process involves treating coal at temperatures of  $\approx$ 360 °C with such solvents as light cycle oil from a fluidized catalytic cracking unit or methylnaphthalene oil (a mixture of 1- and 2-methylnaphthalenes and dimethylnaphthalenes). A flow diagram is shown in Figure 22.1.

1-Methylnaphthalene is a good solvent in this process. Solid–liquid separation is required downstream of extraction, using, e.g. pressure filtration. Removing the solvent from the clarified liquid yields a solid that has virtually the same ultimate analysis as the parent coal, but with very low mineral matter content.

Solvent extraction of bituminous coals using light cycle oil has been developed, originally for production of naphthenic jet fuels having higher volumetric energy density than conventional fuels, in which the dominant components are alkanes. This process operates at 360–390 °C and a residence time of 1 hr. Figure 22.2 shows a flow diagram for this process.

The extraction step uses no hydrogen; the reactor is pressurized to 0.7 MPa (at ambient temperature) so that pressure at working temperatures is adequate to keep



**Figure 22.3** With an abundant source of externally supplied hydrogen, formation of carbon-rich products is effectively shut down, leading to high yields of hydrogen-rich products.

most components from vaporizing. After pressure filtration to remove solids, and distillation to recover and recycle excess solvent, the liquid product is hydrotreated to remove sulfur, and hydrogenated to saturate aromatics. Other clean, middle-distillate fuels can be produced in the same way, including clean diesel fuel or a clean, direct feed to solid oxide fuel cells. If the process is stopped after solvent recovery but before hydrotreating, the liquid product could be a potential feedstock for carbon black production (Chapter 24).

## 22.3 Direct coal liquefaction

#### 22.3.1 Principles

Fischer–Tropsch synthesis of liquids downstream of gasification is called indirect liquefaction because conversion of the coal is actually to a gas, with liquid being made as a separate step downstream. The alternative, direct liquefaction, converts coal to liquids without synthesis gas as an intermediary. The requirement for direct liquefaction can be inferred by comparing H/C ratios of coals and petroleum products. Coal might have an H/C ratio of 0.8, while many petroleum-derived liquids would have values of about 1.8. Conceptually, direct liquefaction could be represented as

$$\mathrm{CH}_{0.8} + \frac{1}{2}\mathrm{H}_2 \to \mathrm{CH}_{1.8}.$$

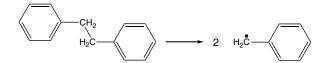
Direct coal liquefaction is sometimes referred to as hydroliquefaction, because of the importance of hydrogen in this approach.

When the "inverted V" diagram was first introduced in Chapter 7, it was said that, in the absence of an external hydrogen source, formation of products of high H/C, such as petroleum-like liquids, must inevitably be accompanied by formation of low H/C products. In most coals the majority of carbon atoms is in aromatic structures, and the H/C ratio is less than 1. The key to avoiding dismal liquid yields from direct liquefaction lies in removing the constraint of "the absence of an external hydrogen source." In the direct liquefaction of coal, much effort goes into supplying an abundant external hydrogen source. (In this context, the term *external* refers to the hydrogen not initially being incorporated in the molecules of the feedstock. Of course, the hydrogen source must be inside the reactor.) The intent is to take the carbon-rich "leg" out of the picture, both figuratively and literally, as in Figure 22.3.

In practice, direct liquefaction has proven very difficult to carry out economically on a large scale. The question of where the external hydrogen comes from cannot be overlooked. Since a direct liquefaction facility must be set up to store, handle, and prepare large quantities of coal, the straightforward approach would make hydrogen by gasification of coal, followed by gas clean-up and shifting. This adds substantial capital cost for the air separation unit, steam generator, gasifiers, shift reactor, and gas treatment. If the gas is shifted all the way to pure hydrogen, there will be an attendant emission of carbon dioxide from the shift reactor, assuming no downstream carbon-capture process. The steadily increasing concern about carbon dioxide emissions from fuel conversion and utilization has caused consideration of alternative strategies. The most likely candidate is production of hydrogen via electrolysis of water using a "non-carbon" electricity source: solar, wind, hydropower, or nuclear.

Gasification destroys completely the macromolecular structure of coal, breaking it into units of one carbon atom, e.g. methane and the oxides of carbon. Since all of the features of the coal are destroyed, in principle at least any rank of coal can be considered for gasification (though not necessarily in practice, Chapter 19). In contrast, direct liquefaction preserves some of the structural features of the coal in the liquid products. The sequence of reactions experienced as the coal structure undergoes liquefaction thus becomes worth consideration.

Converting the macromolecular solid structure of coal to a liquid requires a significant reduction of molecular weight. Vitrinite-rich humic coals have structures that contain aromatic ring systems – usually polycyclic – connected by crosslinks of methylene or polymethylene chains, heteroatomic functional groups, or both. Direct liquefaction is likely to begin with thermally induced cleavage of these crosslinks. Aliphatic C– C bond cleavage in 1,2-diphenylethane (bibenzyl) provides a simple illustration of how a crosslink in the macromolecular structure of coal might break:

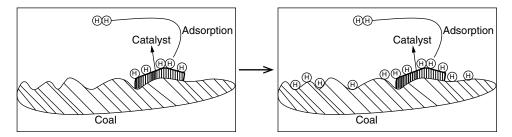


With bond breaking driven by thermal processes, the reactive intermediates are radicals. Reaction occurs at crosslink sites because of the relatively low reactivity of aromatic ring systems compared to aliphatic C–C or C–heteroatom bonds. The temperature requirement to initiate bond-breaking reactions is  $\geq$ 350 °C; many liquefaction processes have run in the range 400–475 °C. Far more stringent reaction conditions would be needed to reduce aromatic rings or for ring-opening reactions.

Breakdown of the macromolecular structure and conversion of coal to soluble products occurs quickly, i.e. in about five minutes. Hydrogen capping is crucial for stabilizing the radicals as quickly as they form,

$$\begin{aligned} \mathbf{R}^{\bullet} + \mathbf{H}_2 &\to \mathbf{R}\mathbf{H} + \mathbf{H}^{\bullet}, \\ \mathbf{R}^{\bullet} + \mathbf{H}^{\bullet} &\to \mathbf{R}\mathbf{H}. \end{aligned}$$

Because the solubility of gases in liquids is inversely proportional to temperature, use of gaseous hydrogen as a reactant requires high-pressure operation, 14–20 MPa [B]. High-temperature, high-pressure operation results in both high capital expense for a plant and high operating and maintenance costs.



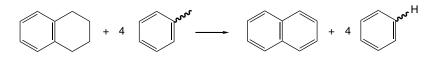
**Figure 22.4** The process of hydrogen spillover involves hydrogen atoms, formed via dissociative chemisorption on the catalyst surface, migrating off the catalyst and onto the coal particle.

Stabilization of radicals by hydrogen capping or by hydrogen abstraction preserves molecular fragments smaller in size than the original coal macromolecule. In direct liquefaction there is – in principle – an unlimited supply of external hydrogen, see Figure 22.3. Repeated bond cleavage and stabilization of radicals with hydrogen converts the macromolecular structure of coal to molecules small enough to be liquids at ambient conditions. Inevitably there is some production of hydrocarbon gases, because it is not presently feasible to control the reaction so precisely that "overcracking" of liquids to gases can be avoided.

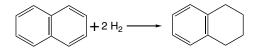
Radical combination reactions, e.g.  $\mathbb{R} \bullet + \bullet \mathbb{H}$ , have activation energies close to zero. Promoting this pathway for hydrogen capping would be helpful. To do so raises the issue of where or how to obtain  $\mathbb{H} \bullet$ . One source is dissociative chemisorption of hydrogen on a catalyst (Chapter 13). This leads to the interesting problem of how to use a heterogeneous catalyst to catalyze reactions of a solid. It could be done effectively by dispersing the active catalyst onto the coal particles [C]. In a sense, the coal acts as a support for the active catalyst. Unlike supported catalysts introduced in Chapter 13, in this case interaction of the catalyst and support is desired. For the catalyst to be effective even though the primary reactant is a solid requires  $\mathbb{H} \bullet$  to migrate from the catalyst to other parts of the coal. This is an example of the phenomenon called hydrogen spillover, see Figure 22.4.

Hydrogen abstraction from another portion of the coal structure stabilizes the reactive radical fragment and generates a new radical site that might be able to react further (by  $\beta$ -bond scission, for example). However, this process leads to no net addition of hydrogen. Hydrogen abstraction can also take place from molecules in the liquid solvent that have abundant hydrogen atoms in positions from which they can be abstracted easily. Such molecules are called hydrogen donors. Tetralin serves as the classic example of a hydrogen-donor molecule, also called hydrogen-donor solvent.

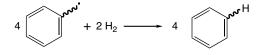
The reaction envisioned for tetralin is



Here the curvy line attached to the aromatic ring is intended to represent generically a molecular fragment produced by breakdown of the coal structure. The four radicals capped by hydrogen atoms from tetralin do not need to be identical. The reaction may proceed sequentially with 1,2-dihydronaphthalene as a transitory intermediate. Hydrogen donated by, or abstracted from, the tetralin caps and stabilizes radicals, facilitating conversion of the macromolecular coal structure to liquids. Tetralin can be regenerated, either *in situ* or in a separate hydrogenation of the solvent:



Recovery of the "spent donor" and its regeneration in a separate step can be accomplished by hydrogenation in a clean reaction with conventional hydrogenation catalysts, such as supported nickel, palladium, or platinum. This provides the way of avoiding having a catalyst in the liquefaction reactor itself. The net process becomes:



The chemical result is still capping of four radicals generated from the coal with four hydrogen atoms, as the equation above shows, but the immediate source of the hydrogen was tetralin.

Assuring a ready supply of  $H\bullet$  at reactive sites as the macromolecular structure of the coal is breaking down helps to intercept an alternative radical reaction, recombination, e.g.  $R\bullet + \bullet R' \rightarrow R-R'$ . Often the products of recombination reactions are less reactive than the parent structures from which they formed. For example, diphenylmethane derivatives are quite unreactive toward further liquefaction. Radical recombination reactions convert the coal into a new solid less reactive than the original coal. In that regard, the liquefaction process might be thought of as running backwards, making a more refractory solid rather than liquids. Recombination reactions that do this are called retrogressive reactions. To maximize formation of liquid products (i.e. to maximize hydrogen abstraction and hydrogen capping) and minimize recombination, enormous ingenuity has been devoted to designing hydrogen donors and catalysts, and to selecting appropriate reaction conditions, to ensure that hydrogen is readily available at, or close to, the sites where free radicals are being generated.

The concept of direct liquefaction was illustrated above by representing coal as a hypothetical  $CH_{0.8}$ . Of course, that is not true. Coals contain oxygen, nitrogen, and sulfur. In direct liquefaction these heteroatoms participate in reactions that consume hydrogen, i.e.

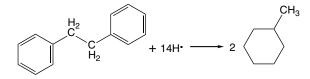
$$\begin{split} \mathbf{O} + \mathbf{H}_2 &\rightarrow \mathbf{H}_2 \mathbf{O}, \\ \mathbf{2} \, \mathbf{N} + \mathbf{3} \, \mathbf{H}_2 &\rightarrow \mathbf{2} \, \mathbf{N} \mathbf{H}_3, \\ \mathbf{S} + \mathbf{H}_2 &\rightarrow \mathbf{H}_2 \mathbf{S}. \end{split}$$

These reactions represent consumption of hydrogen, which has had to be made by an expensive, energy-intensive process that has its own set of by-products and emissions.

#### 22.3.2 Direct liquefaction processing

Feedstocks of choice for direct liquefaction are in the rank range of lignite through high-volatile bituminous. These coals have abundant crosslinks, abundant reactive functional groups, high porosity, and relatively small aromatic ring systems. High-volatile bituminous coals represent the optimum feedstocks. Coals of higher rank are not so reactive. Subbituminous coals and lignites may be more reactive, but their higher oxygen contents require more hydrogen consumption, and loss of carboxyl groups adds to carbon dioxide production. Carbon-sulfur bonds have a lower bond dissociation energy than most other covalent bonds in coals ( $\approx$ 270 kJ/mol for a C–S bond vs. 348 kJ/mol for aliphatic C–C). Such bonds could be places in the coal structure where thermally induced initiation reactions could begin. Pyrite, the common sulfur-containing mineral in coals, converts to the non-stoichiometric compound pyrrhotite, which functions as an active liquefaction catalyst. High-sulfur coals, which are not desirable for combustion or coking applications, could be useful feedstocks for direct liquefaction.

High partial pressures of hydrogen help to drive the reaction  $H_2 \rightarrow 2$  H• on the catalyst surface. Direct liquefaction processes operate at hydrogen pressures of  $\approx 18$  MPa. At the same time, the macromolecular structure of the coal must be undergoing active fragmentation to provide a ready supply of R•. Active thermal decomposition begins around 350 °C. To ensure that reactions proceed at an acceptable rate, and because bondbreaking reactions are endothermic, liquefaction processes typically use temperatures of 400–450 °C. This temperature regime introduces a new complication. Ideally, production of petroleum-like products would involve not only cleaving of crosslinks in the macromolecular coal structure, but also saturation of the aromatic rings. Conceptually,



but, as temperature increases, aromatic compounds tend to become more stable thermodynamically than aliphatics. High temperatures drive bond-breaking, but require high hydrogen pressures and introduce the possibility of "overcooking" the reaction to produce mainly aromatic products. Primary liquid products from direct coal liquefaction generally are highly aromatic, and require further processing downstream of the liquefaction reactor.

Evolutionary development of direct liquefaction since 1945 has led to reductions in reaction severity and improvements in conversion. Conversions can be attained in the 90–95% range (on the basis of dry, ash-free coal) at 15–20 MPa and 425–450 °C. Because active thermal breakdown begins at  $\approx$ 350 °C, this would be about the minimum practical temperature for conventional direct liquefaction processes. A totally different approach to bond-breaking in the coal structure would be needed to achieve significant conversions at temperatures much below 350 °C.

If the principal source of external hydrogen is gaseous  $H_2$ , then liquefaction must be carried out at as high a pressure as practical. Hydrogen has to dissolve into the liquid, a process governed by Henry's law. Solubility is proportional to the partial pressure

in the gas phase, so the higher the pressure, the more hydrogen can be dissolved into the liquid. But also, solubility of gases in liquids decreases as temperature increases. Since direct liquefaction is likely to run at  $\approx$ 400 °C, this gives further reason for high-pressure operation.

Design of catalysts provides several challenges, if the catalyst is to be present in the liquefaction reactor. There must be provision for recovery and regeneration of the catalyst downstream of the liquefaction reactor, unless a very cheap catalyst is used and not recovered. Catalysts of this type are called once-through catalysts, or throw-away catalysts. Any catalyst is vulnerable to poisoning by sulfur, by metals in the inorganic components of the coal, and by coking. Coals are macromolecular solids, and the desirable products of liquefaction are distillable fuels (i.e. gasoline, jet fuel, diesel fuel, and distillate fuel oils), so the catalyst should have good hydrocracking activity. The alternative to finding an active hydrocracking catalyst able to tolerate the effects of possible poisons would be to rely on a hydrogen-donor solvent for hydrogen capping processes in the reaction. The hydrogen-donating ability of the spent solvent could be restored in a separate hydrogenation operation (separate in the sense of not being a part of the liquefaction reactor) that could be run cleanly in catalytic hydrogenation reactors typical of refinery processing (Chapter 15). This alternative tactic does not eliminate the need for hydrogen; it only changes the point in the process at which hydrogen is added.

Realistically, it is never possible to drive a liquefaction reaction to 100% conversion, though under favorable reaction conditions – temperature, pressure, catalyst, solvent, and a highly reactive coal – 90–95% is possible. One of the products leaving the reactor is a sludge of partially converted coal, ash, and the catalyst. It would be difficult and expensive to recover the catalyst from this mess. This problem can be dealt with in at least two ways. One is to use a once-through catalyst. The only catalytically active materials cheap enough to allow considering this approach are compounds of iron. Red mud, a hydrous iron oxide by-product of processing bauxite for aluminum production, and mill scale, mixed iron oxides that form on red-hot steel, provide examples. A second approach uses an alternative source of H $\bullet$ , a source that does not necessarily require a catalyst to be present in the liquefaction reactor, i.e. a hydrogen-donor solvent.

Material leaving the liquefaction reactor is a three-phase mixture of gases, primary liquid products from the reaction, and solids that include the mineral matter from the coal, unreacted or partially reacted coal, and catalyst particles. As the pressure is let down, gases dissolved in the liquid come out of solution and light, volatile components flash to the vapor phase. Loss of these low molecular weight components raises the viscosity of the remaining liquid. All liquids experience an increase in viscosity as the temperature decreases. These two effects result in an increasing viscosity of the liquid, which in turn makes a solid/liquid separation operation very difficult. Experience from direct liquefaction pilot plants in many countries in the 1970s through early 90s suggests that downstream solid/liquid separation is one of the most challenging aspects of practical operation. Possible solutions include use of centrifuges or pressure filters. Alternatively, the entire liquid stream could be distilled, to recover as much distillate material as possible, and the resid, complete with mineral, coal, and catalyst particles, sent to a partial oxidation or gasification process.

The liquid products retain some of the molecular "fingerprint" of the feedstock coal. Unless the liquefaction reaction manages not only to hydrocrack the coal structure but



**Figure 22.5** Friedrich Bergius, inventor of the method for direct liquefaction of coal. Most process development in the field of direct liquefaction since his time involves modifications to, or derivatives of, the Bergius process.

also to saturate aromatic rings and to remove heteroatoms all in the same step, the primary liquid products from direct liquefaction are rich in aromatic hydrocarbons, and aromatic heterocyclic compounds. For these liquids to meet present-day fuel specifications and environmental regulations, additional refining operations are required downstream of the liquefaction reactors. In essence, the primary liquids resemble aromatic, sour crude.

Downstream refining or upgrading processes resemble related petroleum refining processes. Some combination would be used of: distillation; hydrogenation, to convert aromatics to cycloalkanes; hydrocracking, to reduce molecular weight and open rings; and hydrotreating, to reduce concentration of heteroatoms. The same kinds of commercial catalyst and the same reactor designs would be used. The advantage of distilling the primary liquids before further refining is that light products, the candidates for liquid transportation fuels, are usually easier to upgrade than the heavier liquids. Very heavy distillation bottoms or resids would be likely to be used as boiler fuel, or sent to a partial oxidation process for hydrogen generation. Primary coal liquids have higher nitrogen content than the petroleum products. Nitrogen compounds can strongly adsorb to catalysts with acidic sites for cracking or hydrocracking. Deep hydrotreating is needed upstream of other catalytic refining operations to reduce nitrogen to acceptable concentrations.

The earliest practical approach to direct liquefaction, and the only one ever used on a large scale so far, is the Bergius process, see Figure 22.5, [D], of which Figure 22.6 provides a block flow diagram.

Because of the difficulty of introducing solids into a pressurized reactor, pulverized feed coal is slurried in oil. The same tactic is used in gasification, discussed in Chapter 19 with slurry-fed gasifiers. The coal/oil slurry reacts at 475–485 °C. Hydrogen pressure depends on the rank of the feedstock, 25–32 MPa for low-rank coals and  $\approx$ 70 MPa for bituminous. The catalyst is often red mud. The main product, middle oil, is roughly similar to No. 2 fuel oil, and represents about 50% of the liquid. Hydrotreating the middle oil provides gasoline and diesel fuel. The gasoline consists of  $\approx$ 75% alkanes, 20% aromatics, and 5% alkenes, of 75–80 octane. Another 40%

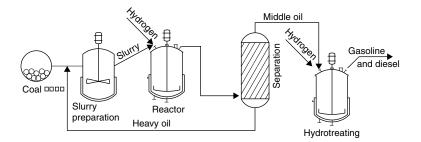
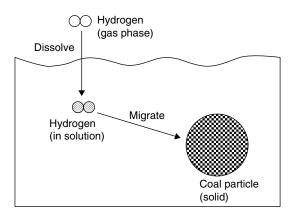


Figure 22.6 Process flow for the direct liquefaction of coal by the Bergius process.



**Figure 22.7** Direct coal liquefaction, especially in the absence of a hydrogen-donor solvent, can involve a three-phase process: gaseous hydrogen must dissolve in the liquid medium, the dissolved hydrogen must migrate through the liquid to a coal particle, and then the dissolved coal must react at the solid coal.

of the liquid is heavy oil, recycled to provide the vehicle for the slurry. Recycling a process-derived liquid has several advantages. Doing so takes advantage of the "like dissolves like" principle of solubility, making it a good solvent for the stabilized fragments of the coal macromolecules. Further trips through the reactor offer the prospect of breaking down some of the components of the heavy oil to lighter products.

The Bergius process involves a three-phase reaction. Gaseous hydrogen must dissolve in the liquid oil, the dissolved hydrogen must migrate through the oil to the coal and catalyst surfaces, and it must dissociate and react at the solid coal surface, as sketched in Figure 22.7.

Most of the research and development work in direct liquefaction over the past 75 years has focused on finding tactics to reduce the temperature, pressure, and residence time requirements for direct liquefaction, exploring modifications to the original work of Bergius [E].

The Exxon Donor Solvent (EDS) process provides an example of a process in which much of the coal conversion relies on a hydrogen-donor solvent. Figure 22.8 provides a simplified flow diagram of the process.

Crushed and dried feed coal is mixed with solvent. The resulting slurry is fed to a dissolver, which is basically a concurrent upward flow entrained-flow reactor. Hydrogen

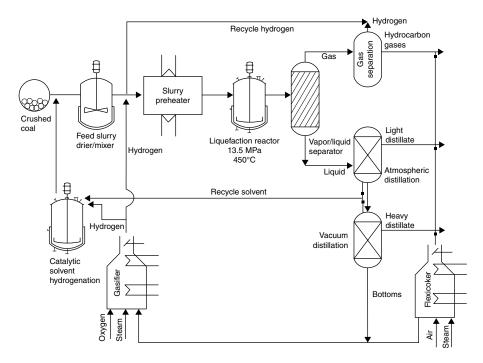


Figure 22.8 Process flow for the Exxon Donor Solvent process.

is also fed at this point, though one of its roles is to continuously re-hydrogenate the solvent, in addition to capping radicals. Reaction temperature is 425-465 °C, pressure 10–17 MPa, and residence time about 45 min. Liquid products are separated by flashing, followed by atmospheric and then vacuum distillation. A 200–425 °C cut of the products is hydrogenated in a separate fixed-bed catalytic reactor before being recycled to the slurry preparation unit. The vacuum distillation bottoms could be converted to hydrogen via partial oxidation, or used to produce additional liquid via Flexicoking (Chapter 16).

Continued process improvements through the 1980s in several countries culminated in the development of two-stage processes employing catalysts in both stages. These were outgrowths of earlier two-stage processes in which one, or both, stages relied entirely on thermal (i.e. non-catalytic) processing. The intent of two-stage processing is to find conditions that reasonably balance several desired outcomes of direct liquefaction: maximizing conversion to distillable liquids, while minimizing hydrogen consumption and production of gases and heavy, resid-like products. Maximizing distillate yield without overcracking to gas requires matching, as closely as possible, the rates of bond breaking in the coal or its primary liquid products with the rate of hydrogen capping.

The Hydrocarbon Technologies, Inc. (HTI) process represents one such catalytic two-stage process [F]. A flow diagram is shown in Figure 22.9.

In the first stage, run at 400 °C, liquefaction takes place primarily by transfer of hydrogen from the solvent to the nascent free radicals from the coal. In the second stage, operating at  $\approx$ 440 °C, the intent is to hydrocrack the heavy liquids, and to

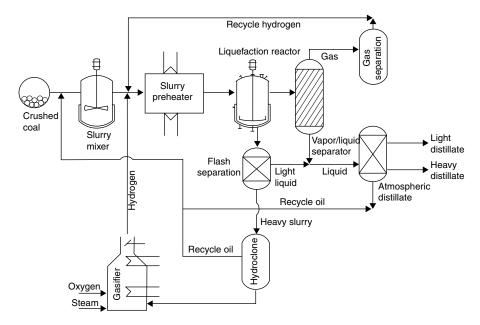


Figure 22.9 Process flow for the H-Coal process.

produce a recycle oil that will be sent back to the first stage. Best results, with high-volatile bituminous coal from Illinois, indicate conversion of 97% on an maf basis, producing about 78% distillate liquids (C<sub>4</sub> to 525 °C). The distillate has low sulfur and nitrogen contents.

Currently the leading effort for commercialization of direct liquefaction is the Shenhua project, in the Inner Mongolia autonomous region of China. The plant uses a modified version of the HTI technology described above. A flow diagram is given in Figure 22.10.

The planned production is three million tonnes of fuel per year, of which about 70% would be clean diesel fuel. The plant is located atop a coal reserve amounting to about two hundred billion tonnes.

Direct liquifaction still faces several challenges (or research and development opportunities, depending on one's point of view). Finding ways to obtain acceptable conversions at lower temperatures and pressures could lead to less expensive reaction vessels and reduced operating and maintenance costs. Reducing reaction severity, and reducing size and number of vessels needed would have a positive impact on process economics. Products of reaction must exit the reactor through some kind of valve. As this three-phase mixture passes through the pressure let-down valve, it can cause erosion of the internals in the valve, leading to remarkably short service life. Separating the solids from the cooling, viscous liquid represents a third challenge to be faced. Although direct liquefaction would not produce so much carbon dioxide as an indirect liquefaction plant,  $CO_2$  emissions still arise from the hydrogen production section of the plant (if gasification is used), from the fired heaters used for processing, and from thermal cleavage of oxygen functional groups in the coal. Clever designs for future processes could incorporate "non-carbon" routes to hydrogen production, and non-

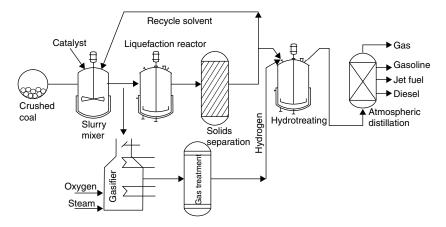


Figure 22.10 Process flow for the direct coal liquefaction operation at the Shenhua plant in Inner Mongolia, China.

carbon sources of process heat, such as concentrated solar, or waste heat from nuclear reactors.  $CO_2$  absorption into algae or other fast-growing biomass would reduce  $CO_2$  emissions and provide a source of bio-oils for blending with coal-derived liquids.

A very different approach to direct liquifaction has involved reacting coal in molten zinc chloride. This remarkable reaction converted coal directly and selectively to highoctane gasoline in one step, with very little of the heavier liquids that accompany the liquefaction processes that derive ultimately from Bergius. Most of the product boils below 200 °C. Nitrogen and sulfur contents of the product are lower than in products of conventional direct liquefaction, by one to two orders of magnitude. The choice of zinc chloride is based on its ability to hydrocrack the macromolecular structure of coal all the way to benzene derivatives. A large quantity of zinc chloride is used, typically about the same mass as that of the coal. The reaction is not without its problems, in that heteroatoms in coal deactivate the catalyst by forming zinc oxide, nitride, and sulfide. Molten zinc chloride is a very aggressive reagent, requiring specialty alloys to avoid dissolving the reactor along with the coal. With continual improvements in tailoring reactivity of molten salts or salt mixtures, and in developing corrosion-resistant alloys, this approach still offers significant potential for reducing or eliminating many of the issues that conventional direct liquefaction processes face. There may prove to be a continuum between low-melting inorganic salts such as ZnCl<sub>2</sub> and organic ionic liquids in this application.

A possible future scenario, particularly in the face of constraints on  $CO_2$  emissions, would find ways of incorporating biomass as a parallel feedstock or as a co-feed. Particularly if biomass is counted as zero carbon, on the basis of its regrowth in each succeeding year capturing the  $CO_2$  emitted from the previous year's crop, then several opportunities are available. First, biomass could be the sole feedstock, or a co-feed, for the gasification section producing the hydrogen. Second, biomass, especially fastgrowing algae, could be used for  $CO_2$  capture (Chapter 25). Using algae to take up the  $CO_2$  from the shift reactors would also allow producing some amount of biofuels from the algae, and feeding the residual solid to the gasifiers. Another option is co-locating a direct liquefaction plant with a nuclear power station. Electricity from the nuclear plant could provide a carbon-free source of hydrogen, via water electrolysis. Depending on reactor design, it could be possible to utilize heat from the reactor to drive the liquefaction reactions and downstream upgrading of the liquids. Both the biomass and nuclear approaches offer strategies for producing liquids from coal with very low  $CO_2$  emissions.

## Notes

- [A] From time to time stories appear on the internet about "free oil" from coal pyrolysis, often in reference to a low-temperature carbonization process developed by Lewis Karrick in the United States some 80 years ago. Many of these stories are accompanied by the usual conspiracy theories, to the effect that the availability of free oil is being suppressed by malevolent government agencies, or a syndicate of oil companies, or both. The Karrick process, and similar carbonization processes, indeed produce a liquid. Presumably, a moderately clever accountant could figure out how this liquid could be "free," provided that markets existed for the rather large amounts of char and gas produced at the same time, and provided that these products could be sold at a price high enough to compensate for giving away the liquid. Then there's the cost of refining the low-temperature tar into specification-grade marketable fuel products...
- [B] Plants running on bituminous coals in wartime Germany supposedly operated with 70 MPa hydrogen pressure. Given the remarkable ability of hydrogen to find, and exploit, the tiniest leaks in piping, seals, valves, or vessels, it seems remarkable that these plants did not blow themselves up, without intervention from the Allied bombing campaign.
- [C] Two practical problems arise. First, most useful liquefaction catalysts, such as  $MoS_2$ , are not soluble in common solvents. To create a fine dispersion of catalyst on coal particles, soluble compounds called catalyst precursors are used. A solution of the catalyst precursor is mixed with coal, the solvent taken off, leaving precursor dispersed on the surface of coal particles. As an example, ammonium tetrathiomolybdate,  $(NH_4)_2MoS_4$ , has been commonly used as a precursor for  $MoS_2$ , presuming that by the time the reaction system has reached  $\approx 400 \,^{\circ}C$  the precursor compound will have decomposed into the catalytically active phase. Second, while much excellent work has been done using dispersed catalysts in the laboratory, it remains to be seen how dispersal of the catalyst precursor would be done in a large, commercial operation liquefying hundreds or thousands of tonnes of coal per hour.
- [D] The process was invented by Friedrich Bergius (1884–1949, Nobel Prize 1931). Bergius has the distinction of being the only fuel chemist to have won the Nobel Prize. He spent six months working in a steel mill before beginning his university education. After his successful development of direct coal liquefaction, Bergius turned his talents and energy to the problem of making sugar from wood, via the acid-catalyzed hydrolysis of wood cellulose. His personal investment in the development work left him in such financial straits that it is said that a bailiff trailed Bergius to Stockholm to collect money from Bergius's Nobel Prize. Because of the importance of the Bergius process to the German war effort, Bergius was not able

to work professionally in Germany after 1945, so he emigrated to Argentina, where he spent the remainder of his life.

- [E] The mathematician and philosopher Alfred North Whitehead once remarked that "All of philosophy is but a footnote to Plato." Most of direct liquefaction is but a series of tweaks to Bergius.
- [F] HTI is now a part of Headwaters, Inc. When the development of the catalytic twostage process began, the company was known as Hydrocarbon Research, Inc. (HRI) and had already developed a reasonably successful single-stage liquefaction process, H-Coal. The H-Coal process relied on ebullated bed catalytic reactors. H-Coal in turn was an outgrowth of an even earlier process, H-Oil, developed for catalytic upgrading of resids and other heavy oil products. This saga exemplifies the intertwining of corporate restructuring and takeovers with evolutionary development of processes that seems to characterize the slow growth of a synthetic fuels industry, at least in the United States.

## **Recommended reading**

- Berkowitz, N. *An Introduction to Coal Technology*. Academic Press: New York, 1979. An excellent introduction to this field. Chapters 6, 7, 13, and 14 contain useful information pertinent to the present chapter.
- Hansen, R. *Fire and Fury*. New American Library: New York, 2008. Numerous history books discuss the importance of the coal-to-liquids effort in Germany during the Second World War, and the impact of the American precision bombing campaign against these plants. This book is a recent and particularly useful addition to such literature.
- Lee, S., Speight, J.G., and Loyalka, S.K. *Handbook of Alternative Fuel Technologies*. CRC Press, Boca Raton, FL, 2007. This book provides a chapter-by-chapter survey of many approaches to making alternative fuels; Chapter 3 is related to the present chapter.
- Probstein, R.F. and Hicks, R.E. Synthetic Fuels. Dover Publications: Mineola, NY, 2006. A highly useful book for anyone interested in this field. Chapters 3 and 6 relate to the present chapter. The Dover edition is a relatively inexpensive paperback reprint of the original version published in the 1980s.
- Ramage, M.P. and Tilman, G.D. *Liquid Transportation Fuels from Coal and Biomass*. The National Academies Press: Washington, 2009. At the time of writing, this book is the most up-to-date review of this topic, at least from the perspective of the U.S. energy economy. It covers technological, economic, and environmental issues.
- Speight, J.G. *The Chemistry and Technology of Coal*. Marcel Dekker: New York, 1994. A very useful reference work; Chapter 16 provides information on a large variety of liquefaction processes.

# 23.1 Thermal decomposition of coals

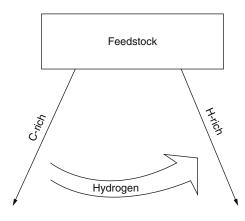
Often the terms carbonization and pyrolysis are used almost interchangeably. Pyrolysis has the broader meaning: breaking apart of molecules by application of heat or thermal energy. As discussed in Chapters 19 and 22, pyrolysis processes could be run to make gases or liquids rather than solids as the primary product. Carbonization, more narrowly defined, refers to conversion of a starting material into carbon, or a carbon-rich solid. It is entirely possible, and indeed often done, to pyrolyze a hydrocarbon feedstock for the purpose of carbonization, but carbonization is not simply pyrolysis by another name. Carbonization can be effected without using heat as the primary driving force, a good example being carbonization of sucrose (ordinary table sugar) by pouring concentrated sulfuric acid on it; carbonization occurs very promptly and very effectively. Carbonization driven by thermal energy usually requires temperatures  $>500^{\circ}C$ .

A carbonaceous solid that appears to have passed through an intermediate fluid state when being produced is called a *coke*. Carbonaceous solids that do not pass through such a fluid state during formation are *chars*. These definitions apply to carbonization processes using any feedstock, including biomass, petroleum, and polymers. All coals, regardless of whether they are caking or coking coals, leave a solid carbonaceous residue at the end of the carbonization process. Chars, if heat-treated to extreme temperatures, e.g.  $\geq 2500^{\circ}$ C, do not form graphite, while cokes do. That is, chars are non-graphitizable, while cokes are graphitizable [A].

A carbon-rich solid and lighter, comparatively hydrogen-rich gases or liquids result from carbonization. In principle, carbonization could be run to produce any one of these as the desired products. Again it is helpful to consider the "inverted V" diagram, Figure 23.1.

Without an external source of hydrogen, carbon-rich materials necessarily are produced, because their formation serves as the source of "internal hydrogen" for production of hydrogen-rich products. The low atomic H/C ratio of coal, usually <1, indicates that carbon-rich products will dominate in this system. This is not to imply that formation of carbon-rich products is necessarily a bad thing. Deliberate formation of a carbon-rich product is the crux of the second-most important commercial use of coal, production of metallurgical coke.

Reaction severity, predominantly temperature, drives processes downward on the inverted V diagram. Pyrolysis of coal usually proceeds in three distinct stages. Stage 1 occurs below 200°C. The principal volatile products come from loss of



**Figure 23.1** The formation of carbon-rich products, such as coke, is inevitably accompanied by some hydrogen-rich products (gases and tars), resulting from transfer of internally available hydrogen.

functional groups; they include water, carbon dioxide and monoxide, and hydrogen sulfide. Water probably comes from dehydration of clay minerals and of organic functional groups, e.g.

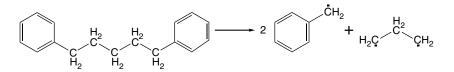
$$R-CH_2-CH_2-OH \rightarrow R-CH=CH_2+H_2O_2$$

Carbon oxides arise from thermal decomposition of oxygen functional groups, e.g.

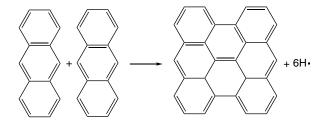
$$R-CH_2-COOH \rightarrow R-CH_3+CO_2$$
,

and from driving off oxygen that had chemisorbed on the coal surface during exposure to air. Stage 1 reactions tend to be slow.

Stage 2 occurs in the temperature range 350–550°C. Products are light hydrocarbon gases, such as methane, ethane, and ethylene, as well as a great variety of organic compounds that condense to a complex mixture called coal tar. In this stage, aliphatic carbon–carbon and carbon–oxygen bonds that form bridges between aromatic ring systems break apart. A hypothetical example might be

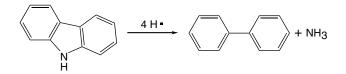


This example leads to propane in the gaseous products and toluene and 1,2-diphenylethane (bibenzyl) in the condensable liquids. Structural fragments too large to escape with the volatiles undergo radical recombination reactions to form larger, even more carbon-rich, structures. As a hypothetical example, anthracene could experience dehydrogenative polymerization:

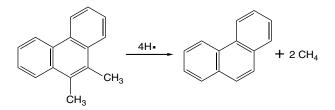


H• formed from dehydrogenative polymerization could help stabilize hydrogen-rich products. The solid material produced when starting with lignite, subbituminous coal, or anthracite is char. The special case of bituminous coals is discussed later. As might be anticipated from Figure 23.1, when small, hydrogen-rich molecules are evolved during active thermal decomposition, the system has also started moving directly toward carbon-rich solids as the other product; i.e. carbonization has begun.

Stage 3, which begins above 550°C, produces various small gaseous molecules, including water, carbon monoxide and dioxide, hydrogen, methane, ethane, ethylene, acetylene, and ammonia. The residue is a solid of high carbon content. These small gaseous products are formed because larger molecules are now being torn apart thermally



and side chains are being removed from aromatic ring systems:



This is a regime of fierce thermal decomposition. The solid product becomes increasingly carbon-rich, and in principle could proceed all the way to carbon if heating is continued to temperatures over 2000°C. Normally this process would not produce graphite, because the carbonaceous char does not have long-range, three-dimensional structural order.

# 23.2 Low- and medium-temperature carbonization

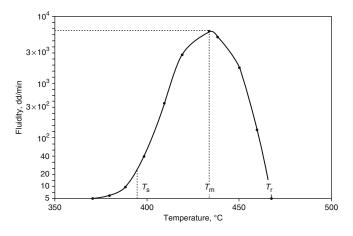
Three variations of carbonization have been developed. Low-temperature carbonization occurs in the range 450–700°C. Carbonization in this range maximizes the yield of tar. Application of various separation and extraction processes to the tar yields a large number of useful chemical products. The gas produced during low-temperature carbonization is useful as a fuel. The remaining carbonaceous solid, usually called char, can also be highly reactive and a useful fuel. Medium-temperature carbonization is run at 700–900 °C. This temperature range maximizes the gas yield, providing a potential route to a gaseous fuel. The char is also a useful fuel, sometimes sold as a smokeless fuel. High-temperature carbonization occurs at 900–1200 °C. The principal product is a hard, porous coke for use in blast furnaces in the metallurgical industry. High-temperature carbonization is by far the most important of the three processes, and is discussed in more detail in later sections of this chapter.

While the various carbonization retorts differed in size, internal design, capacity of coal, and mode of operation, generally all were batch processes running at 500–700 °C on lump coal, requiring anywhere from four to sixteen hours per charge. Necessarily carbonization is accompanied by production of gas and tar. A good business operation would market all the products. The Krupp–Lurgi process in Germany produced liquid transportation fuels and fuel oil in addition to the coal char. The Rexco process, first commercialized near Nottingham in Britain, produced about 700 kg char, 80 l of tar (for further refining), and 700 m<sup>3</sup> of a low calorific value (5 MJ/m<sup>3</sup>) gas per tonne of coal. Most of the low- and medium-temperature carbonization processes became obsolete with the increasing availability of petroleum products, natural gas, and electric heating after World War II.

An important application of carbonization was production of smokeless solid fuels. Especially in Great Britain and Europe, with high population densities in cities, use of coal for domestic heating and cooking, and in small industrial or commercial sites, resulted in significant air pollution problems, due to smoke and to sulfur emissions [B, C]. Carbonizing coal at 500–700 °C drove off most of the volatiles and much of the sulfur, leaving char that was much cleaner burning than the original coal. Some of the solid, smokeless fuel products were sold under various trade names, such as "Phurnacite," "Homefire," and "Coalite."

# 23.3 The special case of bituminous coals

When most bituminous coals pass through the region of Stage 2 thermal decomposition, the non-volatile material softens into a plastic state, swells, and then resolidifies into a single piece, rather than remaining as a pulverized material in a condition similar to the original coal sample. This phenomenon is not a true melting, because melting is a reversible phase transition, and what happens to bituminous coals is definitely not reversible. Coals that show this behavior are referred to as being caking coals. Caking behavior is unique to the bituminous rank and often is especially strong with the medium-volatile coals. A special subset of the caking coals resolidifies to a hard, strong, porous coke, the fuel used in metallurgical processes. The most important application of coke is in the smelting of iron ores in blast furnaces. Those caking coals that can be used to produce coke are known as coking coals. Generally, good coking coals are of medium-volatile and low-volatile bituminous rank. They command a premium price in the coal market relative to coals burned for making steam in electric plants (the so-called steam coals). Coking coals must be caking coals. However, not all caking coals produce good coke, so a caking coal is not necessarily a



**Figure 23.2** A Gieseler fluidity curve. Softening and resolidification temperatures correspond to the points at which the curve crosses 20 dial divisions per minute. The temperature of maximum fluidity corresponds to the peak of the curve.

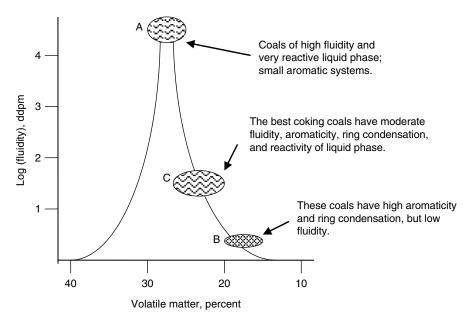
coking coal. As a rule, the good coking coals are in the range of 18–32% volatile matter on a dmmf basis.

The free swelling index (Chapter 17) provides a good, relatively simple, screening test for caking or coking behavior. It does not provide a complete characterization, which must come from additional tests measuring fluidity and plastic properties. Further characterization of the plastic stage involves measuring the fluidity of the plastic mass and the change in volume that occurs. Fluidity is measured using a Gieseler plast-ometer. In this device, a stirrer is immersed in a mass of solid coal of  $\leq$ 425 µm particle size. With a constant torque applied to the stirrer shaft, the speed of revolution of the stirrer is measured while the coal is being heated at a rate of 3°C per minute. Fluidity data are expressed in units of dial divisions per minute (ddpm). Figure 23.2 is an example of a Gieseler fluidity curve.

Three temperatures are read from the fluidity curve. The temperature at which fluidity first becomes 20 ddpm is the softening temperature,  $T_s$ . Fluidity passes through a peak at the temperature of maximum fluidity,  $T_m$ . Further heating above this temperature results in the plastic mass becoming less fluid. At the resolidification temperature,  $T_r$ , fluidity has decreased back to 20 ddpm. One other parameter, the plastic range, is determined from  $T_r - T_s$ .

Figure 23.3 displays the relationship of Gieseler fluidity to coal rank.

This relationship is usually expressed using volatile matter on a dry, mineral-matter-free (dmmf) basis as the indicator of rank. Coals of highest fluidity (Point A) are not necessarily ideal coking coals. These coals,  $\approx 30\%$  dmmf volatile matter, are high- and medium-volatile bituminous rank. From Figure 17.3, they would be expected to contain appreciable oxygen,  $\approx 10\%$ . Destruction of oxygen functional groups during Stage 2 thermal decomposition generates large numbers of radicals, resulting in a very reactive liquid phase. These coals have low values of aromaticities and ring condensation indices. Coals at Point B are highly aromatic with large condensed ring systems, but fluidity may be too low to allow extensive alignment in the liquid. The best coking coals, C, represent a compromise between fluidity, aromaticity, ring condensation, and reactivity of the liquid.



**Figure 23.3** The best coking coals represent a compromise between moderate fluidity and reactivity in the fluid state with aromaticity and ring condensation.

The volume change accompanying the plastic stage is measured in a dilatometer. The sample is compressed into a rod, and placed in the dilatometer beneath a piston, the other end of which has a scale indicator. Changes in volume during heating can be monitored by recording the position of the indicator. Three parameters characterize dilatometric behavior. Contraction, C, is a shrinkage occurring in the early stages of heating. Swelling, S, is the change in volume from the lowest point measured during contraction to the maximum observed volume. Dilatation, D, is the permanent change in volume when the sample has resolidified, relative to the volume of the original unheated sample. Commonly, the dilatation behavior of a coal is measured as a function of temperature while the sample is being heated at a constant rate. An alternative, but more laborious, study is to heat coal to a constant temperature and measure the dilatation as a function of time, collecting data for a series of temperatures. Figure 23.4 provides an example of results of a dilatometry experiment.

The plastic behavior of coals can be assigned to one of four classes, subplastic, euplastic, perplastic, or fluidoplastic, as Figure 23.5 shows.

The usefulness of dilatometry lies in the fact that coals of the same FSI can have very different dilatometric behavior. Expansion and contraction of the coal in its plastic state relates to, e.g., the pressure that would be put on the walls of coke ovens, which in turn could significantly impact the safety of their operation.

# 23.4 Chemistry of coke formation

The extent of solvent swelling (Chapter 17) relates to the number of crosslinks per chain segment, the so-called crosslink density. Crosslink density of a coal can be estimated by measuring the extent to which it swells in various solvents. Crosslink density decreases

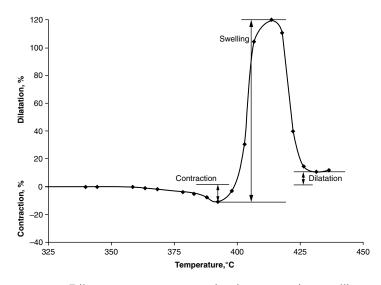
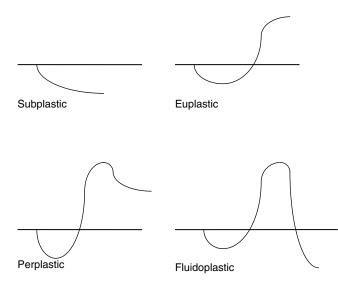


Figure 23.4 Dilatometry measurement, showing contraction, swelling, and eventual dilatation.



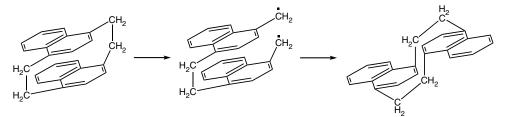
**Figure 23.5** The major types of dilatation behavior observed with coals. The x-axis in each case is temperature, and the vertical distances represent percent contraction or percent dilatation, following Figure 23.4.

as rank increases, and appears to be at a minimum around 88–90% carbon. Bituminous coals are the least crosslinked of the various ranks of coal. Anthracites represent a different case, in that, at about 90% carbon, the ring condensation index, R, shows a very steep increase (Figure 17.7). With very large values of R in anthracites, these coals may have extensive  $\pi$ - $\pi$  interactions. Coking coals are found in the region of coal rank where the cohesive energy, whether covalent crosslinks or strong  $\pi$ - $\pi$  interactions, of the solid is near a minimum.

In addition to being the least crosslinked, bituminous coals generally show a comparatively high population of hydroaromatic structures. These compounds have been discussed previously (Chapter 22) in connection with their role as hydrogen-donor molecules. When a bituminous coal is heated into Stage 2 thermal decomposition, crosslinks break, as in any other coal. In many coals, the newly generated radicals undergo rapid recombination. But, in the coking coals there is not a large number of crosslinks that need to be broken. When the relatively few crosslinks do break, the resulting radicals can be capped by "internal" H• from hydroaromatic structures. Hydroaromatic structures can stabilize radicals by transferring labile hydrogen to the radical. In a sense, bituminous coals pass through a fluid phase during Stage 2 thermal decomposition because they liquefy themselves.

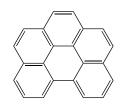
Large molecules thermally cleaved from the coal structure and stabilized by hydrogen donation could function in the coal the way a plasticizer does in a polymer. In polymers, a plasticizer is a nonvolatile solvent that stays between the macromolecular structures (e.g. polymer chains) and acts like a "molecular ball bearing" by reducing intermolecular interactions, and making it easier for the polymer to flex or elongate. In coals, the plasticizer is called metaplast, which provides a fluid phase inside the coal, specifically providing mobility to large aromatic structures, allowing them to move, align, and rearrange into a strong, stable, coke structure. Eventually, with continued heating, radical generation, and internal hydrogen transfer, even the hydrogendonating ability of the hydroaromatic structures is overwhelmed, leading the entire mass to solidify into coke.

The cyclophane compound syn-[2.2)(1,4)-naphthalenophane provides a possible model for the structural rearrangements in coking coals. This compound has  $f_a$  of 0.83 and R of 2, comparable to, say, high-volatile A bituminous coal. This cyclophane melts at 240°C, and undergoes a resolidification at 250°C to form the anti- isomer, probably via the formation of a diradical intermediate:



In this rearrangement, the two naphthalene rings must somehow slip past each other. In a coal, the movement of one aromatic ring system (possibly of higher R values) past another could be facilitated by the metaplast.

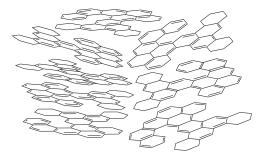
Bituminous coals that particularly display this behavior are in the rank range where the ring condensation is likely to be in the range of four to six. As the coal self-liquefies, the liquid contains molecules like dibenzochrysene (23.1a):



23.1a Dibenzochrysene



23.1b Edge-on view of dibenzochrysene



**Figure 23.6** Represents the short-range order in the fluid phase. The molecules, likely to be mostly aromatic rings with some naphthenic rings and some heterocycles, align over short distances and with different orientations.

Viewed edge-on, such molecules appear relatively flat, e.g. 23.1b. A liquid containing such structures has maximum fluidity when the molecules are roughly aligned, producing short-range order in the liquid phase, see Figure 23.6.

This produces a material in which there is some ordering, as might occur in a solid, yet overall retains the characteristics of a liquid. These so-called liquid crystals represent an extremely important phase of matter [D]. Because of the formation of a liquid crystalline state, the resulting cokes generally have more ordered structures than chars. This helps explain why cokes can be converted to graphite, whereas chars usually cannot.

Liquid crystals exist because of a balance between intermolecular forces (for aromatic molecules, the interactions of the  $\pi$  electron systems) and the rotational and translational energies of the molecules. In a solid, intermolecular interactions provide sufficient cohesion to overcome rotational and translational energy that would allow the molecules free movement. In an ordinary liquid, molecules have enough energy to overcome the intermolecular forces of the solid and to have sufficient freedom of motion so that liquid is isotropic. In a liquid crystal, substantial intermolecular forces still exist, making the material crystal-like in this respect, but are not strong enough to prevent flow, making the material also liquid-like. The anisotropic liquid crystal precursor to coke formation is mesophase.

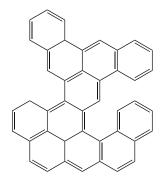
Making an anisotropic, graphitizable coke from coal requires formation of an anisotropic mesophase. If, instead, the fluid formed during carbonization is an isotropic liquid, the resulting solid is an isotropic char. An isotropic liquid phase forms at the onset of thermal breakdown of the macromolecular structure of the coal. Reactivity of the liquid phase is determined by the concentration of radicals in the liquid. If hydrogen redistribution is difficult, the radicals are likely to experience recombination, rather than hydrogen abstraction or hydrogen capping. If the molecular-scale distribution of radicals is random and isotropic, formation of new C–C bonds by radical recombination proceeds in random directions. The structure of the solid that eventuates from this process is also isotropic, because C–C bond formation has occurred in all directions.

If the liquid first formed from the coal can undergo internal hydrogen redistribution that allows capping radicals, the total population of radicals in the liquid is reduced, and the liquid has less reactivity than the case just discussed. The less reactive liquid phase tends to be of lower viscosity (i.e. higher fluidity). Higher fluidity allows the molecules in the liquid the mobility to align; lower overall reactivity gives molecules the chance to align before they are consumed in recombination reactions. This situation provides the potential for dehydrogenative polymerization reactions, illustrated above for anthracene. Of course, compounds present in the actual liquid from the thermal breakdown of coal are more varied and more complex than anthracene. Dehydrogenative polymerization of a mixture of compounds could give rise to such structures as benzoperylene (23.2).



23.2 Benzoperylene

Structures from dehydrogenative polymerization of anthracene have a high lengthto-breadth ratio and, in two dimensions, present a rod-like appearance. They align in the liquid phase to form nematic liquid crystals. Ordering in a nematic liquid crystal, where the aromatic ring system was viewed from the side, almost edge-on, is illustrated in Figure 23.6. Molecules likely to form from dehydrogenative polymerization of the mixture of compounds present in coal tar are also nearly flat, but with little difference between the length and breadth of the molecule. As structures of this kind continue to grow, they become roughly circular. These roughly circular structures form discotic nematic liquid crystals. A hypothetical structure might be that of 23.3, where some of the rings in this molecule might be hydroaromatic structures, rather than fully aromatic. Discotic nematic liquid crystals constitute the mesophase. Extensive growth of ring systems would be needed to form a discotic mesophase. The discotic molecules that eventually produce this liquid crystal phase are called mesogens. Similar effects have long been known in the field of colloid chemistry, where so-called mesomorphous substances contain large molecules joined in ordered structures even in the fluid phase.



23.3 Hypothetical liquid crystal structure

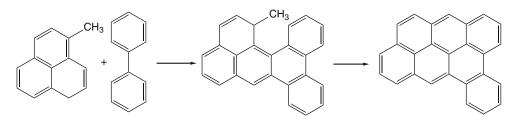
For systems in which reactivity has been reduced by hydrogen capping of some of the radicals, the growth of molecules is slow enough so that molecular size does not increase significantly until high temperatures are reached. But, since the fluidity of a liquid increases with increasing temperature, the point at which molecular growth

becomes significant is at, or near, the point at which fluidity is high. This allows the mesophase to continue to accommodate more molecules of mesogens and, consequently, continue to grow.

From the onset of active thermal decomposition to  $T_{\rm m}$ , the coal is liquefying itself. Crosslinks are being broken and the nascent free radicals are being capped by H• from hydroaromatic groups. Thermal decomposition produces metaplast. Metaplast is unstable toward further thermal decomposition. Thermal cracking of metaplast produces a solid material, sometimes called semicoke, and a variety of volatile compounds, both gases and condensable tars:

#### Metaplast $\rightarrow$ Semicoke + Gases and Tar Vapors.

The fluid metaplast, the plasticizer, allows the structural components of the mesophase to rearrange and grow in the fluid state, and to undergo condensation reactions that might be represented by the formation of tribenzochrysene:



In these reactions, the hydrogen liberated could be utilized internally to drive hydrogen redistribution.

With continued heating, components of the metaplast evaporate, or pyrolyze, to produce volatile compounds. Their vapors bubble through the plastic mass, causing it to swell. Radical recombination and dehydrogenative polymerization produce everlarger aromatic structures in the liquid, reducing fluidity. As the fluid resolidifies, the tracks left by the bubbles of volatiles and gases passing through the fluid do not fill with fluid. When most of the metaplast is gone, the residue resolidifies. Thus

Metaplast  $\rightarrow$  Gases + Semicoke.

At higher temperatures, the semicoke continues to react, by dehydrogenative polymerization, by loss of methyl groups from methylated aromatic structures, and by loss of hydrogen. Methane and hydrogen evolve as further gaseous products as semicoke transforms to coke:

## Semicoke $\rightarrow$ Coke + Gas.

Semicoke retains some elastic nature up to about 700°C. With further heating, to about 1000°C, it transforms into hard, brittle coke. The transformation is usually accompanied by shrinkage, probably due to the continuing growth of large aromatic structures and their alignment into graphite-like crystallites.

Petrographic analysis is very important for evaluating coal quality for coke making. The petrographic components of coals can be classified as "reactives" and "inerts." The former category contains vitrinite, exinite, and some semifusinite. The behavior of passing through a fluid state with evolution of volatiles in the way just described is characteristic of vitrinites of bituminous rank, of about 78–89% carbon. Liptinites are

	Aliphatic		Aromatic	
Number of carbon atoms	Compound	Melting point, degrees C	Compound	Melting point, degrees C
10	decane	-31	naphthalene	80
14	tetradecane	6	phenanthrene	100
16	hexadecane	20	pyrene	150
18	octadecane	28	chrysene	254

**Table 23.1** Comparative melting points of some simple aliphatic and aromatic hydrocarbons.

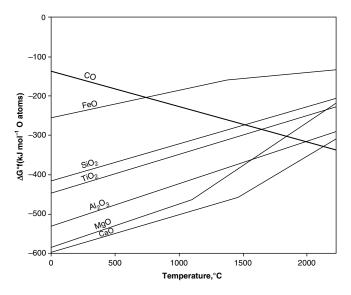
mainly aliphatic, whereas vitrinites are more aromatic. Compounds having the same number of carbon atoms show substantial differences in melting points between aliphatic and aromatic compounds. The data in Table 23.1 illustrate this.

Liptinites might be expected to become fluid at lower temperatures than the more aromatic, and possibly more crosslinked, vitrinites. Sporinite becomes fluid at slightly higher temperatures than vitrinite, but becomes very fluid and loses much weight as volatiles before it resolidifies. In small amounts, sporinite can contribute usefully to the fluidity. Resinites (in the exinite group) begin to soften as low as 200°C, softening and vaporizing in the range 200–300°C. Vitrinite macerals become plastic around 350°C, begin to develop a coke structure in the range 425–500°C, and solidify by 700°C. Other exinite macerals become very fluid at about the temperature at which the vitrinites first begin to develop a coke structure, i.e.  $\approx$ 425°C. The inerts include fusinite, other inertinite macerals, and some forms of semifusinite. Fusinites or micrinites do not become fluid at any rank, but concentrations up to 25% of these macerals can increase the strength of the resulting coke, probably in the same way that adding aggregate to cement makes a strong concrete. Mineral matter also is included with the inerts.

Many factors affect the plastic behavior of coal. While these effects are well established by empirical observation, how and why these factors produce these effects is not clearly understood on a fundamental level. Increasing the heating rate increases the temperature of maximum fluidity, the maximum fluidity itself, and the swelling. Oxidation of the coal (e.g. from prolonged exposure to the atmosphere during long-term storage) reduces maximum fluidity, free swelling index, and the plastic range. Heating bituminous coals to  $\approx 200$  °C and holding at that temperature largely destroys their caking behavior. In contrast, heating coal in hydrogen can improve these same properties. Fine grinding of coal decreases the plastic behavior; reducing the ash yield improves it. These very diverse empirical observations make it difficult to develop a single mechanism of plastic behavior that incorporates them all into a comprehensive conceptual framework. Mineral matter content in excess of about 10% reduces the caking properties, probably by a simple dilution effect of its being an inert constituent in the fluid phase.

## 23.5 Industrial production of metallurgical coke

Early in human history, forerunners of today's metallurgists learned that carbon, often in the form of charcoal, was very useful in liberating metals from their ores. Smelting of iron ore goes back at least 2500 years. The usefulness of carbon in this application stems



**Figure 23.7** The Ellingham diagram plots the thermodynamic stability of oxides as a function of temperature. The key feature is the negative slope of the curve for carbon monoxide. In principle, it would be possible to find some temperature at which carbon could reduce any oxide.

from a curious relationship of the temperature dependence of free energies of formation. The Ellingham diagram [E], see Figure 23.7, shows this.

The Ellingham diagram plots the standard free energies of formation of various oxides as a function of temperature. A given element will reduce any of the oxides that lie above it on the diagram; for example, chromium would reduce zinc oxide. The remarkable feature, however, is that the free energy of formation of carbon monoxide becomes increasingly negative as temperature increases. In the absence of other considerations any metal oxide can be reduced with carbon, given a high enough temperature, i.e. past the crossover point on the Ellingham diagram. In other words, carbon could serve as a universal reducing agent for all other oxides. Unfortunately, there is one "other consideration:" that some metals form very stable carbides, so reducing their oxides with carbon would produce the corresponding carbides rather than the free metals [F].

Before the eighteenth century, the preferred carbon source was charcoal, produced by carbonization of wood. It works exceptionally well in this application [G]. Consumption of wood was prodigious, some 1.5 to 3 hectares of trees needing to be felled per tonne of iron produced. Ironmakers turned to coal as a substitute for charcoal. Direct use of coal gives a poor grade of iron, because  $H_2S$  volatizing from the coal enters the molten metal, precipitating iron sulfide in the boundaries between the metal grains. When the iron is reheated to be worked into a useful shape, it can tear or break along these weakened grain boundaries, spoiling the metal piece. At the same time, brewers tried using coal as a substitute for charcoal to dry the hops and malt used for making beer. A similar problem ensued: volatiles from the coal ruined the flavor of the resulting beer. Brewers discovered that heating coal in the absence of air drove out the volatiles, leaving a solid that still had considerable value as fuel – coke. Ironmakers



Figure 23.8 Beehive coke ovens.

quickly learned that coke was an excellent fuel and reducing agent for iron furnaces. The development of the modern blast furnace operating on coke is attributed to Abraham Darby, his furnace going into operation in 1709 [H].

The first approach to coke-making borrowed from charcoal practice: a heap of coal was prepared, with pieces of wood running through it. The wood was set on fire; the heat liberated was intended to carbonize the coal. Clearly, issues of process control, consistency of product quality, and environmental impact were not considered. A significant improvement came from enclosing the coal in a dome-like structure in which much of the process heat derived from burning the volatiles emitted as the coal experienced carbonization. Someone's notion that these structures looked like behives led to the name beehive coke oven (Figure 23.8).

Beehive ovens produce good quality coke. However, the discovery of the first synthetic dye, mauve, in 1856, from allyltoluidine, obtained from coal tar [I], grew to the realization that it would be better to recover the products of coal carbonization for use as chemical feedstocks, rather than burn them inside the beehive oven. A new coke oven design, the by-product recovery coke oven, was developed. The visual appearance of this oven resulted in its also being called the slot-type coke oven (Figure 23.9).

Sizes of slot-type ovens vary, but they could be 15 m long and 6 m high. In practice, some 20–100 individual ovens are built side-by-side in a coke oven battery. Flues between each pair of ovens provide a place for gas, from the carbonization, to be burned to supply heat for the coking process. The very narrow width of each oven, typically  $\approx$ 50 cm, is governed by limitations on heat transfer, to ensure that heat can penetrate completely to the center of the charge. Coke ovens are batch reactors; the time needed for coking a charge of coal is typically 18–24 hours.

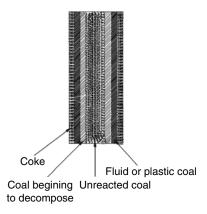
The feedstock to a coke oven needs to have a number of special properties: high free swelling index ( $\approx 6-7$ ), high fluidity, wide plastic range, and low mineral matter content. Mineral matter in the coal could dilute the metaplast, interfering with the growth of large aromatic ring systems. Phosphorus, sulfur, and silicon should have low concentrations in the mineral matter, because if these elements were carried into the coke and from there into the metal, they could harm the quality of the metal.



Figure 23.9 A battery of slot-type coke ovens, also known as by-product recovery ovens.

Individual coals that meet all the requirements of a good coking coal are becoming scarce [J]. They command a premium in the marketplace relative to steam coals. Modern practice involves blending coals so that it is the blend that meets the requirements, rather than any single coal. Over the course of the twentieth century the amount of coke required to produce one tonne of metal, the coke rate, has decreased from seven tonnes per tonne to less than one. Even so, the difficulty of obtaining single sources of good coking coals is such that large steelmaking complexes might draw on multiple mines as coal sources. At least one coal in the blend must be a good coking coal. Sometimes a weakly caking coal, or even a non-caking coal, could be blended with a high-swelling, highly fluid coal to create a blend with good coking properties. Various rules of thumb have been developed to establish the criteria of a "good" blend; one such recommends a fluidity of 200-1000 ddpm; ash value 6.0-8.0%; sulfur, 0.7-1.0%; and phosphorus, 0.01-0.03%. Radical changes in the fluid, swelling, and/or dilatometric parameters could lead to severe damage to the ovens in a battery. If maximum fluidity is too great, or if dilatation is too great (especially for strongly euplastic coals), enough pressure can be built up to damage or destroy the oven walls. Therefore coal blends are very carefully and very thoroughly evaluated in test ovens before being accepted for use in the commercial battery.

In a slot-type oven, the charge is coked from the walls inward (Figure 23.10). The various layers – coke, plastic coal, and partially decomposed coal – move toward each other from the walls, so that at the end the whole mass of charge has been converted to coke. A rule of thumb is that the time to coke a charge of coal is one hour per 2.5 cm of furnace width. Coking is complete when the solid coke forms all the way through the oven. At that point the oven is "pushed" with a hydraulic ram to move the coke out of the oven. Individual coke pieces have a length equivalent to about half the width of the oven. The coke is a very carbon-rich, highly aromatic, strong, porous solid. The porosity arises from gases bubbling through the plastic coal as the volatiles escape during carbonization. It is highly aromatic because Stage 3 thermal decomposition occurs in a temperature region where aromatic carbon is the thermodynamically stable form of carbon (Figure 23.11).



**Figure 23.10** The situation inside a slot-type coke oven when the charge has partially coked. Coking begins from the walls and proceeds inward toward the center.

The coking pressure, i.e. the pressure applied to the walls of an oven by the charge, is generated as the plastic coal swells and pushes the remainder of the solid charge against the walls. Coking pressure depends on several parameters, including fluidity of the plastic layer, its thickness, and the rates of evolution of volatiles as coking proceeds. Coking pressure is measured in a test oven of which one wall is free to move. As a rule, wall pressures below 14 kPa are considered safe; higher pressures are dangerous.

The amounts of products coming from a coke oven depend on the composition of the coal(s) charged to the oven. Generally, each tonne of coal fed to the ovens produces about 750 kg of coke,  $350-400 \text{ m}^3$  of coke-oven gas, 10-15 kg of light liquids (mainly benzene, toluene, and the xylenes), 30-40 kg of tar and 2-5 kg of ammonia. Water production, as an aqueous solution of ammonia and small organic molecules, depends on the moisture content of the coal. Coke-oven gas contains high concentrations of hydrogen, carbon monoxide, and methane, which provide a high calorific value, making a useful fuel gas. Its primary use is to be burned in flues between each individual oven in a battery; the walls of the ovens reach  $1300^{\circ}$ C. If additional gas is available, it can be used elsewhere in the plant, or sold to off-site users.

The dominant market, accounting for  $\geq 90\%$  of coke production, is in blast furnaces for reduction of iron ore. Coke serves at least three roles in a blast furnace. Combustion provides heat needed for the endothermic processes of melting metal and slag. Combustion also produces carbon monoxide, the primary reducing agent responsible for conversion of iron oxides to iron metal. Additional carbon monoxide comes from the Boudouard reaction of carbon dioxide with coke. A blast furnace is a metallurgical parfait, consisting of successive layers of coke, iron ore, and limestone (added as a flux to produce a low-melting, low-viscosity slag). Coke must also have the mechanical strength to support all the layers of charge above it, while providing permeability for gas flow upward and for downward flow of metal and slag. Coke produced from coal has several additional, but relatively small, markets, such as production of calcium carbide for acetylene manufacture.

The preferred composition of blast furnace coke would be < 1.5% volatile matter, < 10% ash, <0.12% phosphorus, and <1.0% sulfur, with a calorific value  $\ge 33.7$  MJ/kg.

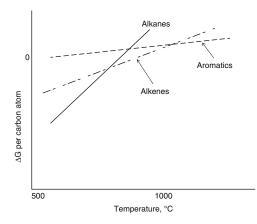


Figure 23.11 As temperature increases, aromatic carbon becomes more stable (in terms of  $\Delta G$  per carbon atom) than paraffinic or olefinic compounds.

Coke reactivity is assessed by measuring the behavior of a sample when heated in air, oxygen, carbon dioxide, or steam under standardized test conditions. A variety of such tests has been developed; the data from different tests do not seem to correlate with each other or with fundamental coke properties. Nevertheless, results of such tests can be related to coke performance in the blast furnace, sometimes by relying on prior experience with cokes of similar reactivities measured in the same test. For use in blast furnaces, coke must also meet specifications for hardness and for resistance to abrasion. Various tests have also been devised to measure these physical properties and relate the values obtained to coke performance.

High-temperature tar produced as the by-product from coke making is a rich source of organic chemicals. For at least 75 years, from the development of by-product coke ovens until the ready availability of inexpensive petroleum after World War II, coal-tar chemicals were a major feedstock for the chemical industry. This era was a glorious chapter in the histories of coal technology and of industrial organic chemistry. In the second half of the twentieth century, "carbochemicals" gave way to petrochemicals. The fact that chemical by-products might amount to only  $\approx 5\%$  of the amount of coal fed to the ovens did not help. Steady progress in reducing the coke rate in blast furnaces, and changes in steelmaking technology (e.g. to electric arc furnaces [K]) result in reduced coke demand and production, which directly relates to reduced production of coal-tar chemicals. Further, coke and coal tar plants, as built to the environmental standards of 50 or more years ago, were redolent with the difficult-to-forget fragrances of hydrogen sulfide, pyridine, phenols, and polycyclic aromatic hydrocarbons. It is questionable whether many industrialized countries would allow environmental permitting of a new by-product coke oven battery today. Indeed, because of environmental concerns, an emerging trend is the construction of "non-recovery" ovens that resemble the beehive ovens of a century ago, with provision for burning the volatiles inside the oven. This is not to say that there is no future for specialty chemicals derived from coal. The challenge and opportunity lies in developing entirely new processes for producing valuable chemical products, but ones that do not require high-temperature carbonization in coke ovens.

## Notes

- [A] This distinction may depend on the temperature of heat treatment. Anthracites, for instance, have been considered to be non-graphitizable, and this seems to be the case at temperatures of roughly 2000–2500°C. However, above ≈2800°C, at least some anthracites produce good quality graphite.
- [B] In 1272, Edward I, King of England, banned the burning of sea coal (so called because it was brought by sea from the northeast of England) in London because of complaints about air quality. Richard III and Henry V also tried limiting or eliminating the burning of coal (obviously Edward's ban had little effect, despite his declaration that burning of coal was a capital offense). Four hundred years after Edward, John Evelyn, best known today for his long and detailed diary of seventeenth-century life, published *Fumifungium*, the first book describing problems of air pollution from coal combustion.
- [C] Air pollution related to coal combustion in domestic and small commercial appliances continued well into the twentieth century, notably so-called sulfuric acid smog. The worst disaster associated with this form of pollution occurred in London in 1952, when several thousand people died prematurely as result of being exposed to this acidic smog, and many tens of thousands were made ill. In recent years the emerging field of medical geology has come to recognize severe human health consequences from chronic exposure to smoke from coal fires, especially in poorly designed domestic stoves or heaters. Some of the hazardous trace elements in coals, such as arsenic and mercury, can be volatile at the temperatures of combustion; they move from the coal to the smoke to the inhabitants of the house, with possibly serious long-term consequences.
- [D] As their name implies, liquid crystals combine properties of two states of matter. Liquid crystals have short-range order that would be typical of a crystalline solid, but have the ability to flow, pour, and adapt to the shape of the container that characterizes liquids. Among a great many applications of liquid crystals, there are digital watch and calculator displays, video games, and high-definition television.
- [E] Named in honor of the English thermodynamicist and electrochemist Harold Ellingham (1897–1975). Ellingham spent his career at Imperial College. Aside from his many contributions to science, during World War II he served as a member of Imperial's Air Raid Precautions group, for protecting personnel and buildings during air raids.
- [F] As an example, titanium forms a very stable carbide, so the carbon reduction of titanium oxide is not a practical route to producing this very useful metal. In fact, iron also forms a stable carbide, Fe<sub>3</sub>C. Much of the practical, industrial work in the metallurgy of iron and steel involves efforts to eliminate, reduce, or somehow manipulate this carbide phase in the metal.
- [G] Charcoal still finds uses in metallurgy. It is the preferred reducing agent when very pure metal or a specialty alloy is desired. It is also a viable option when biomass is abundant but coking coal is not. Operations in Brazil and in Australia show the feasibility of combining a forestry operation with a metallurgical plant, so as to convert some of the biomass to charcoal for use in metal production.
- [H] Abraham Darby (1678–1717) first operated his furnace on "charked coal" in January 1709, in Coalbrookdale, a village in Shropshire in the West Midlands of

England. That year, the furnace produced about 80 tonnes of iron. Darby's development of the practical blast furnace probably represents the beginning step of the Industrial Revolution.

- [I] This discovery was made by William Henry Perkin, who was 18 at the time. He was trying to synthesize quinine, an important antimalarial medicinal compound, from allyltoluidine. Perkin's discovery was the first step in establishing an enormous organic chemical industry, based heavily on raw materials obtained from coal tar. Like Darby's seminal work on the blast furnace and its effect on the Industrial Revolution, Perkin's discovery of mauve was probably the first key step in establishing the organic chemical industry.
- [J] Coking coals have had roles in determining the outcome of wars. In World War II, the invading German armies captured the Donets Basin, a region with large deposits of excellent coking coals inside the Soviet Union. Hitler forbade the German army to give up this territory (and the coals) when the Soviets counterattacked, even though prudent strategy would have been to straighten out the defensive lines. As a result, large bodies of German troops were trapped and captured or annihilated. Had they been able to withdraw and fight elsewhere, they might have made a difference in the outcome of other battles, and perhaps of the war.
- [K] A remarkable irony, and great research and development opportunity, is that the graphite electrodes used in steelmaking arc furnaces are made from two raw materials: petroleum coke and coal-tar pitch. Coal-tar pitch is a distillation residue from processing of high-temperature tars from coke ovens. Increasing use of electric-furnace technology reduces the demand for coke, which reduces the production of coal-tar pitch, which causes shortages of a vital raw material needed to make the electrodes for the furnaces an interesting embodiment of the law of unintended consequences. A need exists for producing coal-tar pitch suitable for making graphite electrodes without needing a coke oven, or for finding a suitable pitch made from other feedstock.

#### **Recommended reading**

- Alvarez, Ramón and Díaz-Estébanez, María-Antonia. Chemistry of production of metallurgical coke. In: *Sciences of Carbon Materials*. (Marsh, Harry and Rodríguez-Reinoso, Francisco, eds.) Universidad de Alicante Publicaciones: Alicante, 2000; Chapter 18. This chapter is a good and reasonably up-to-date introduction to cokemaking.
- Berkowitz, Norbert. *An Introduction to Coal Technology*. Academic Press: New York, 1979. This book remains a very useful and informative introduction to this topic. Chapters 6 and 11 contain material relevant to the present chapter.
- Brock, William H. *The Norton History of Chemistry*. Norton: New York, 1992; Cardwell, Donald. *The Norton History of Technology*. Norton: New York, 1995. These companion volumes provide interesting historical background on coal tar chemicals, and on Darby and the blast furnace, respectively.
- Gray, Ralph J. Coal to coke conversion. In: *Introduction to Carbon Science*. (Marsh, Harry, ed.) Butterworths: London, 1989; Chapter 9. This work discusses the formation of coke largely from the perspective of what can be learned from optical microscopy, including petrographic analysis of coals.
- Komaki, Ikuo, Itagaki, Shozo, and Miura, Takatoshi. *Structure and Thermoplasticity of Coal.* Nova Science Publishers: New York, 2005. An edited collection of contributions from

various authors, probably the most up-to-date collection of fundamental scientific investigations of coal softening, plasticity, and coking.

- Lankford, William T., Samways, Norman L., Craven, Robert F., and McGannon, Harold E. *The Making, Shaping, and Treating of Steel.* United States Steel: Pittsburgh, 1985. The most comprehensive monograph on steel metallurgy. Chapter 4 treats coke-making and recovery of by-product chemicals.
- Loison, Roger, Foch, Pierre, and Boyer, André. *Coke: Quality and Production.* Butterworths: London, 1989. A comprehensive and detailed monograph on production of metallurgical coke.
- Van Krevelen, D.W. *Coal: Typology Physics Chemistry Constitution*. Elsevier: Amsterdam, 1993. An excellent and comprehensive treatment of coal science, the best available. Chapters 23 and 24 relate to the present chapter.

# 24 Carbon products from fossil and biofuels

Charcoal, petroleum cokes, coal, chars, and metallurgical coke are produced to be used as fuels, or in metallurgical applications as reducing agents. This chapter discusses production of other carbonaceous solids that find use because of their special properties as solids, not as fuels or as reducing agents. Premium carbon materials can be sold at prices well above the cost of the feedstocks, sometimes several US dollars per kilogram. Production and sale of such materials, even as by-product associated with a larger fuel conversion or refining operation, represents a significant revenue source.

# 24.1 Activated carbons

Activated carbons derive from a variety of feedstocks, including wood, coal, agricultural products, and peat. The usual method of production involves carbonizing the feedstock and reacting the char (either subsequently or simultaneously) with a reactive gas, to develop porosity and a high degree of internal surface area in the solid. Activated carbons have a wide range of uses in the adsorption of impurities from liquid or gas streams, including many applications in environmental protection or remediation.

Two strategies, physical or chemical activation, are used for production of activated carbons. These terms are commonly accepted and used in the activated carbon field, but unfortunately are slightly misleading, in that both rely on chemical reactions, albeit of different sorts. Physical activation begins with carbonization. Then, in a second, separate processing step, the char undergoes partial gasification, usually by reaction with steam or carbon dioxide. This gasification step actually does the activation, opening or creating porosity in the carbon, and increasing its internal surface area. In chemical activation, the feedstock is impregnated with a dehydrating agent that will degrade cellulose, such as phosphoric or sulfuric acids, and zinc chloride. The impregnated feedstock is then carbonized; during carbonization the added reagent decomposes part of the feedstock structure, thereby creating or opening internal porosity. Washing the reagent out of the now-activated char at the end of the carbonization step leaves the activated carbon.

Three main physical forms of activated carbon are produced. Granular and powdered activated carbons differ in terms of particle size. Various associations or societies have slightly different standards for discriminating between the two forms; one example specifies that material for which 95–100% passes a 0.177 mm (i.e. 8-mesh) sieve is powdered activated carbon, larger material being granular. Their production, regardless of the activation process, is illustrated in Figure 24.1.

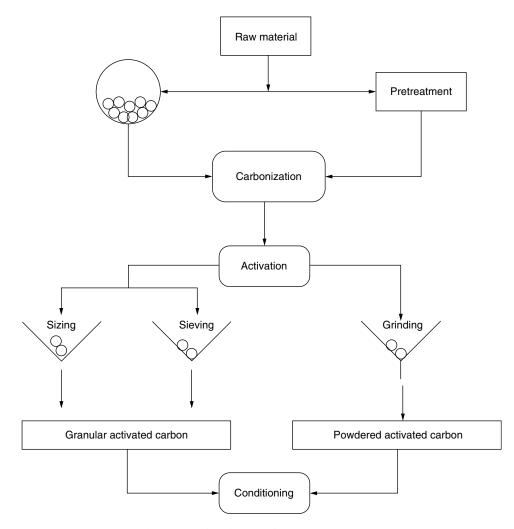


Figure 24.1. Process flow for activated carbon production.

The third form, pelletized activated carbon, incorporates additional processing steps. The feedstock is crushed or ground to fine particle size, mixed with a binder, such as coal tar, and then extruded into pellets. The pellets are carbonized and activated by physical activation processes, or can be treated by chemical activation. Regardless of the form of carbon produced, the intended application of the product may require some modification of the chemical nature of its surface, such as the incorporation of oxygen functional groups (discussed below). In that case, the final processing step is a conditioning of the carbon by appropriate reaction.

Activated carbon can be made from many kinds of feedstock, including fossil-fuel sources such as petroleum coke and every rank of coal, and biomass sources such as peat, wood, agricultural residues (e.g. fruit pits and nut shells), and charcoal. The choice of feedstock has a major effect on the nature of the carbon produced; different feedstocks, even processed under identical conditions, yield activated carbons with different physical and chemical properties. However, the same feedstock, when processed under different conditions, can also yield carbons of very different properties. This means that, given a

supply of a particular feedstock, the appropriate combination of activation procedures and conditioning can allow "tailoring" the final carbon to meet a desired application.

Pores in activated carbons are classified into three types, on the basis of width or diameter (assuming a roughly circular cross-section). Micropores have widths <2 nm. A distinction is sometimes drawn between narrow micropores (<0.7 nm) and wide micropores (0.7–2 nm). The next larger are the mesopores, 2–50 nm. Macropores are larger than 50 nm. Activated carbons have pores in all three size classifications. Most of the adsorption occurs in the micropores. The meso- and macropores provide passages, or serve as "feeders," for adsorbates to reach the micropores. Controlling the relative distributions of pores among the three types provides a way of tailoring the performance of the activated carbon.

Gas adsorption is the most common approach to measuring the surface area of an activated carbon. Several gases, including nitrogen and carbon dioxide, have been used in this application. Also, several models exist for calculating the surface area from the empirical gas adsorption data, such as the BET model (Chapter 13). A sample of activated carbon displays different values of surface area, depending on the gas adsorbate and the method of working up the data. This calls into question what the "true surface area" of an activated carbon really is, or indeed whether the notion of a true surface area has any meaning. The recommendation has been made always to use the term "apparent surface area," since what is being measured and reported is only a surface accessible to a specific gas under certain experimental conditions. And, surface area data reported without reference to the gas and calculation method used are useless. Activated carbons may contain closed pores, i.e. internal voids that do not connect to, or are not open to, the external surface of the particle. Gas adsorption measures only the surface area in the open pores, i.e. ones that connect to the surface of the particle.

The BET method (Chapter 13) represents a standard approach to interpreting gas adsorption data on carbon materials, but its extension to microporous solids is questionable. The BET method presumes that the adsorbate accumulates on the surface by building up layer by layer. This is not very likely in a micropore. The Dubinin–Radushkevich (DR) method provides an alternative for analyzing adsorption data on microporous solids. One form of the DR equation is

$$V = V_0 \exp(-\varepsilon/E)^2.$$

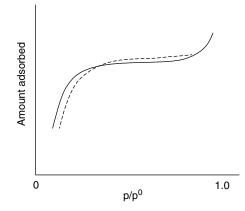
Here  $V_0$  is the micropore volume; V, the volume of gas adsorbed; E, an energy term; and  $\varepsilon$ , the adsorption potential, is given by  $RT \ln(p^0/p)$ , where  $p^0$  is the saturated vapor pressure of the adsorbate and p the measured pressure in the experiment.

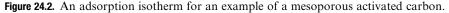
In mesoporous carbons, the adsorbate forms a meniscus in the pore; the curvature of the meniscus affects the adsorption and desorption behavior of the adsorbate. The isotherm (i.e. plot of amount of gas adsorbed as a function of relative pressure  $p/p^0$ ) shows hysteresis over some range of  $p/p^0$ . Figure 24.2 provides an example for a hypothetical mesoporous carbon.

Hysteresis can be exhibited by mesopores having irregular shapes or random constrictions, or by ink-bottle pores (Figure 17.2). The mean radius of the mesopores,  $r_k$ , can be found from a version of the Kelvin equation

$$r_{\rm k} = 2\,\sigma V_{\rm m}/RT\ln(p^0/p),$$

where  $\sigma$  and  $V_{\rm m}$  are the surface tension and molar volume of the adsorbate liquid, respectively.





Macropores are often characterized by mercury porosimetry. This technique forces mercury into pores at high pressures. Mercury is assumed not to wet the pore walls, so would have a convex meniscus inside a pore. The pressure needed to force mercury into a pore of radius r can be found from the Washburn equation

$$r = 2\sigma\cos\theta/\Delta p$$
,

where  $\sigma$  is the surface tension of mercury;  $\theta$  is the contact angle between mercury and the pore surface, usually assumed to be 140°; and  $\Delta p$  is the difference between the pressure applied to the liquid mercury and the pressure of the gas occupying the pore. Porosimetry results provide a measurement of cumulative pore volume distribution as a function of pore radius.

In physical activation, type of furnace and its operating conditions – i.e. heating rate, final temperature to be reached, and residence time at the final temperature – affect yield of char and, to some extent, development of porosity. Porosity development is enhanced in the subsequent activation step. The carbon–steam reaction and the Boudouard reaction (or both) are responsible for developing porosity. As discussed in Chapter 19, these are endothermic reactions. Rates are unacceptably slow below  $800 \,^{\circ}$ C. For a specific char, in which some pore development has already occurred during carbonization, steam activation provides a distribution of pore sizes that includes contributions from meso- and macropores, whereas carbon dioxide activation tends to develop the microporosity. Air could also be used as an activating agent, but in this case the key reaction is the rather exothermic carbon–oxygen reaction. Consequently, it is difficult to keep this reaction under control and to arrive at a desired distribution of pore sizes.

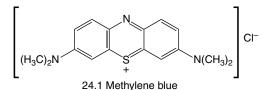
Chemical activation processes usually rely on peat or wood as the feedstock. Activation is run at 400–700 °C, usually in a rotary kiln. Using a reagent such as zinc chloride at relatively small loadings, e.g. <0.3% by weight, usually produces a microporous carbon with only a small amount of macroporosity. This is because the small reagent loading can provide a very uniform distribution of the activating agent throughout the feedstock. It is not so easy to obtain a uniform distribution with a larger amount of reagent, so the resulting carbons show greater contributions of meso- and macroporosity.

The discussion of gas–carbon reactions (Chapter 19) pointed out that edge sites in an extended array of carbon atoms are more reactive than sites in the basal plane. The reactivity of a given carbon is determined by the relative populations of reactive edge atoms and less reactive basal plane atoms. The adsorption behavior of activated carbons is analogous. A higher population of edge atoms relative to basal plane atoms provides greater opportunities for chemisorption, particularly of oxygen. Graphite does not make a good adsorbent; the basal-plane atoms dominate in graphite. A good activated carbon has a much less ordered structure than does graphite, and consequently a higher population of edge atoms.

The other principal way of controlling adsorption performance of an activated carbon is through the surface composition of the carbon. A variety of chemical treatments will modify the surface of a carbon by introducing oxygen or nitrogen functional groups. The acidity or basicity of these groups in turn affects the kinds and amounts of species that will adsorb on the surface. Most oxygen functional groups known to occur in aromatic structures have been postulated to occur on the surface of carbons treated with oxidizing agents. In addition to oxygen itself, many other reagents have been used to create oxygen functional groups on the surface of carbons. Examples include nitrous and nitric oxides, ozone, nitric acid, and hydrogen peroxide. Characterization of surface functional groups is usually done by Boehm titration. The procedure involves a series of four titrations, beginning with sodium bicarbonate, to react with carboxylic acid groups. Titration with sodium carbonate measures carboxylic acids and lactones; with sodium hydroxide, carboxylic acids, lactones, and phenols; and finally sodium ethoxide, which would react with all of these groups and carbonyls. Subtracting the results of one titration from another then gives values for each of the four functional groups.

Most activated carbons contain some inorganic material, usually determined as a percentage of ash after burning off the carbon. If nearly pure hydrocarbon feedstocks are used, the ash value can be quite low, e.g. < 1%. Biomass feedstocks, which include wood, or agricultural residues such as pits from fruit or shells from nuts, could produce carbons with 1–4% ash. When coals are the feedstock, the resulting carbon could have >10% ash. The inorganic components of the carbon could have some role in modifying the adsorption behavior, either by interacting directly with the adsorbate or by affecting the interaction between the carbon and the adsorbate.

Characterization of adsorptive properties of an activated carbon is done using one or more standardized tests. Iodine number, expressed as milligrams of iodine adsorbed per gram of carbon, is a useful probe of internal surface area in a carbon. For many carbons the iodine number agrees fairly closely with the apparent surface area determined by gas adsorption. The methylene blue number, the number of milliliters of a standardized solution of methylene blue (24.1) decolorized by 0.1 g of carbon, shows how well the carbon sample would adsorb large molecules.



439

The phenol adsorption test measures the weight percent of phenol adsorbed on a carbon from a solution of 10 mg/l phenol, when the final concentration is reduced to 1 mg/l. Phenol adsorption is especially useful for characterizing carbons to be used for water treatment.

Most of the physical properties of activated carbons are measured to help design or operate practical adsorption devices. Bulk density, the mass of carbon filling a unit volume of air, is used to estimate the packing volume in an adsorption unit; apparent density (measured by mercury pycnometry), the mass of a unit volume of the carbon particles themselves, then allows determining the bed porosity, and hence flow characteristics, in a packed-bed adsorber. Measurements of mechanical strength indicate how well the carbon particles will stand up to attrition during handling and use.

Activated carbons enjoy a multitude of uses in both liquid-phase and gas-phase treatment operations. Gas-phase applications include, as examples, removing gasoline vapors from air, sweetening of sour gas, and air separation, i.e. oxygen from nitrogen. Current interest in abating mercury emissions from coal-fired power plants offers a potentially enormous market for activated carbons. Most gas-phase applications use granular or pelletized carbons.

Liquid-phase operations mainly rely on both granular and powdered carbons. The major market in this area is in water treatment. This application includes both drinking water treatment before use, and wastewater treatment before the water is discharged back to the environment. One concern for drinking water treatment is the removal of compounds that might be injurious to health; another is to make the water palatable by removing compounds that would cause objectionable tastes or odors. The latter application also provides markets for activated carbons in the beverage and food industries. Wastewater treatment potentially involves dealing with a wide array of possible pollutants. Activated carbons are used to treat both municipal and industrial wastewaters. Either type of wastewater could be a complex mixture of compounds: detergents, pesticides, sugars and starches, dyes, solvents, proteins, fats, hydrocarbon oils, and drugs provide a few examples. Liquid-phase applications of activated carbons could also extend to fermentation processes; these are not limited to ethanol production, but are finding increasing application in preparation of a range of biochemical materials such as vitamins and antibiotics.

For economic or environmental reasons, or sometimes both, it is often desirable to regenerate the activated carbon once it has reached the limit of its adsorption capacity. Doing so allows the carbon to be re-used, and the adsorbed materials to be disposed of properly. Regeneration can be effected by heating the "spent" carbon in an unreactive gas atmosphere, or in superheated steam. Sometimes a simple pressure reduction can remove adsorbed gases from a carbon. More complicated regeneration operations might require extracting an adsorbate using some appropriate solvent, then leaving the question of what to do with the solution of extract.

## 24.2 Aluminum-smelting anodes

The standard method of obtaining aluminum from its ores is the Hall–Héroult process [A]. The principal ore of aluminum is bauxite, impure aluminum oxide and oxyhydroxides, usually mixed with oxides of iron, silicon, and sometimes titanium. Bauxite is purified by the Bayer process, which involves leaching with aqueous sodium hydroxide. Aluminum oxide readily dissolves:

$$Al_2O_3 + 2 NaOH + 3 H_2O \rightarrow 2 NaAl(OH)_4$$

The other oxides do not dissolve, leaving behind a sludge that is colored red because of the presence of hydrous iron oxides or hydroxides – the very same red mud that could be used as a throwaway catalyst in direct coal liquefaction (Chapter 22). After filtering off the insoluble material, the solution is treated with carbon dioxide to precipitate aluminum hydroxide, or a hydrous form of aluminum oxide:

$$NaAl(OH)_4 + CO_2 \rightarrow Al(OH)_3 + NaHCO_3$$

Collecting the aluminum hydroxide and calcining it generates a purified form of aluminum oxide:

$$2 \operatorname{Al}(OH)_3 \rightarrow \operatorname{Al}_2O_3 + 3 \operatorname{H}_2O_2$$

Aluminum oxide is dissolved in molten sodium hexafluoroaluminate, Na<sub>3</sub>AlF<sub>6</sub>, commonly known by its mineral name, cryolite. The bath is molten at  $\approx$ 960 °C. At the cathode, aluminum ions are reduced:

$$\mathrm{Al}^{+3} + 3 \, e^- \to \mathrm{Al}.$$

Molten aluminum collects at the bottom of the cell, from which it can be withdrawn periodically. The anode reaction is commonly written as

$$\mathrm{C} + 2 \,\mathrm{O}^{-2} \rightarrow \mathrm{CO}_2 + 4 \,e^-,$$

though the actual oxygen species is probably not the free oxide ion, but rather complex species such as  $(Al_2O_2F_4)^{-2}$ .

The net reaction in the production of aluminum is

$$2\operatorname{Al}_2\operatorname{O}_3 + 3\operatorname{C} \to 4\operatorname{Al} + 3\operatorname{CO}_2.$$

The stability of aluminum carbide,  $Al_4C_3$ , precludes direct reduction of aluminum oxide with carbon. The stoichiometry of this reaction predicts a carbon requirement of 0.33 kg per kg of aluminum produced. In industrial practice, the actual consumption is 0.4–0.6 kg C/kg Al. About two-thirds of the carbon consumption is due to the direct reaction of carbon with oxygen released from decomposition of aluminum oxide. Most of the remainder is due to two processes. One is the Boudouard reaction, carbon dioxide reacting with carbon. The other comes from the fact that these anodes are hot when in use, and a portion of the anode is exposed to air above the molten electrolyte bath. This provides a second, albeit much smaller, avenue for oxygen attack on the anode. Loss of carbon resulting from exposure of the hot anode to air is sometimes called air burn.

Two key raw materials are used to manufacture the anodes needed for aluminum smelting. One is a carbonaceous solid, called a filler. The other is something that can be used to "glue" the particles of filler together into a coherent body; this material is called a binder. For anode manufacture, the filler is usually sponge coke (Chapter 16). Coke is calcined at  $\approx$ 1250 °C to effect further carbonization and to drive off volatile components that have somehow survived the coker. When an anode has been consumed to a

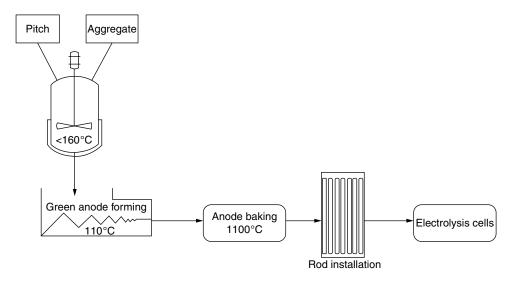


Figure 24.3. Process flow for production of anodes for aluminum smelting.

point at which it must be replaced, some of the original anode material remains. Rather than waste them, these residual pieces of anode – known in the trade as butts – are used with coke as filler material. The binder is coal tar pitch, the distillation residue of coal tar as produced in metallurgical coke ovens. The mixture consists of approximately 15% pitch, 65% calcined coke, and 20% butts. Mixing is done at about 50 °C above the temperature at which the pitch softens; usually around 160 °C. A flow diagram for anode production is given in Figure 24.3.

After the mix has been prepared, it is cooled to about 10 °C above the softening point of the pitch. Then, it is formed into a "green" [B] anode of about 1 tonne. The green anode undergoes baking at  $\approx$ 1100 °C for three weeks [C]. The resulting baked anode is attached to electrically conducting rods that, in the common design, fit into holes molded into the anode during its manufacture. To ensure a good electrical contact between the rods and the anode itself, and to ensure mechanical rigidity, the rods are held in place by pouring molten iron into the hole around each rod. What is, at this point, called a rodded anode is the device that actually goes into the electrolysis cell. A typical cell has 24 of these 1 t anodes. A production facility consisting of multiple cells is called a pot line; a pot line might have about 250 cells. In other words, at any given time a single pot line in one facility will account for some 6000 t of anodes, which each have a lifetime of about three weeks.

An alternative technology involves Soderberg electrodes, sometimes referred to as selfbaking electrodes. Soderberg electrodes can be used in aluminum manufacture, but also in other metallurgical applications, such as making ferrochrome alloy. For these electrodes, a mixture of pitch and coke is fed into one end of a steel casing. The other end opens into the furnace. As the pitch–coke mixture approaches the hot end of the casing (i.e. approaches the interior of the furnace), it begins to bake. Baking is completed as the mixture is extruded into the furnace itself. Soderberg technology is a bit simpler than using pre-baked anodes, since separate anode-baking units are not required, and fresh anode is continuously available without needing to shut down to replace anodes.

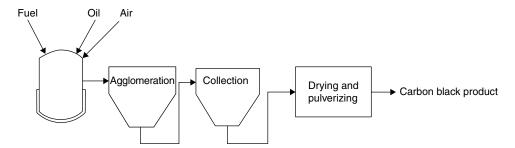


Figure 24.4. Process flow for production of furnace black.

In any electrolytic cell, an anode needs a cathode. In aluminum smelting, the cathode blocks are often manufactured with anthracite as the filler. Penetration of sodium into the cathode, as might happen with a cathode made from petroleum coke, could result in swelling of the cathode and eventual mechanical failure. A well-made cathode lasts about five years, in marked contrast to the three-week life of an anode.

# 24.3 Carbon blacks

Carbon blacks are colloidal, usually spherical, particles or aggregates of spherical particles. There are hundreds, if not thousands, of commercial grades of carbon blacks marketed worldwide, differing in porosity and surface chemistry, as well as particle size and aggregate size or shape. As produced, carbon blacks have bulk densities as low as  $0.06 \text{ g/cm}^3$ . Particle size ranges from 10 to 1000 nm. Carbon blacks have several commercially valuable uses, including the black powder in xerographic and toner cartridges, the pigment in printing inks, and a filler in rubber and other polymers to enhance resistance to wear and abrasion. About 25% of the weight of a rubber tire is actually carbon black; in fact, this is why tires are black. Commercial carbon blacks have a variety of trivial names, reflecting their specific method of production and feedstock. Carbon blacks are made from the incomplete combustion of natural gas, fuel oil, or coal tar fractions. The yield of carbon black depends on how they were made, and from what feedstock, but often is about 2 to 6%.

The dominant production process is the oil furnace process (Figure 24.4). The process begins by igniting a flame of natural gas or oil in the presence of excess air. The feedstock oil, a highly aromatic by-product of petroleum refining or coal processing, is injected into the flame. Carbon black forms at the point where the feedstock hits the flame. Water cooling occurs almost immediately after the carbon black forms. The carbon black is then collected on bag filters. Up to this point, the residence time for carbon black in the furnace is about 1 s at most. Depending on the intended application, the carbon black powder is pelletized to allow easier handling and less dust formation. Furnace blacks account for about 75% of carbon black production, and are used to improve tensile strength, tear resistance, and abrasion resistance of rubber and other polymers. Particle size is in the range 30 to 80 nm.

Pyrolysis of an oil product or natural gas leads to thermal blacks. The feedstock enters a hot (1400–1650 °C), brick-lined generator, where it pyrolyzes to carbon black

and hydrogen. After 2–3 min, the generator is purged with steam to remove the product, which again is water-quenched and collected on a filter. While this carbon black production is taking place, some of the feedstock is being burned in a parallel generator to heat the interior. Thus thermal black production represents a switching back and forth between two parallel units, one of which is being heated while the other is in use for making the carbon black. Among the various kinds of carbon blacks, thermal blacks tend to have the largest particle size, up to 500 nm, but form small aggregates. Particle sizes of 200–500 nm take them out of the range of practical use for rubber reinforcement, but the thermal blacks have uses in making wire insulation, electrodes for batteries, and, in the previous century, carbon paper.

Acetylene black is made by thermal decomposition of acetylene. The reaction chamber is preheated to  $\approx 800$  °C, at which point acetylene is introduced and undergoes an exothermic pyrolysis [D]. Because the pyrolysis is exothermic, the temperature inside the reactor reaches  $\approx 2500$  °C. Carbon black formation takes place from the time the acetylene is introduced to a temperature of about 2000 °C. Further reaction in the range 2000–2500 °C induces partial graphitization of the carbon black. Due to their partially graphitic nature, acetylene blacks have specialty applications where good conductivity of electricity or heat is needed, or where a very low chemical reactivity is desirable.

Two other processes find use to a limited extent. Channel blacks are produced by burning natural gas in a limited supply of air. The carbon deposits in cold iron channels (hence the name) that slowly reciprocate past scrapers, so that the deposited carbon is scraped off the channels and collected in hoppers. The yield is quite low, typically 2–6%. Channel black particles, 20–30 nm in diameter, have uses as pigments in high-quality printing inks and as additives for rubber used in large truck tires. Production of lampblack dates from antiquity; it is made by burning a feedstock, such as an aromatic oil, in a limited supply of air. Persons with kerosene lamps or lanterns for camping, or for use as back-up in the event of electricity failure, sometimes produce lampblack inadvertently when the fuel-air ratio is not adequately adjusted in the lamp. Lampblacks made deliberately by modern processes are in the 70–100 nm diameter range and are usually highly aggregated.

Carbon blacks have a totally aromatic structure, i.e.  $f_a$  of 1.00. Instead of having the perfect alignment of aromatic layers as in the graphite structure, carbon blacks do not have long-range structural order. The microstructure consists of small "packets" of turbostratic crystallites [E], not aligned with each other. The structural order depends on the method of preparation. Atomic planes near the surface tend to align parallel to the surface. In graphite, interactions among the  $\pi$  electron systems of each aromatic plane provide the weak bonding between planes. Because the aromatic planes are not aligned in carbon blacks, the weak  $\pi$ - $\pi$  interactions can be fulfilled by adsorption of gases, such as oxygen. Channel blacks may contain 12–18% of material that volatilizes on heating to 1000 °C. The strong chemisorption of gases on carbon blacks is also partly responsible for their ability to reinforce polymers, e.g. rubber. In this process, the carbon black particles must be small,  $\approx$ 20–50 nm, and able to be wetted by the polymer, implying that there must be relatively strong surface interactions between the components of the polymer and the surface of the carbon black particles.

Many properties of carbon blacks are important in their characterization and in the specific application to which they are put. Those most important are particle size, size and shape of the aggregates, porosity, and the chemistry of the carbon surface.

Particle size, in a range of very small sizes characteristic of carbon blacks, is measured by transmission electron microscopy. The sizes and shapes of aggregates can also be studied by this method. The aggregates usually form in complex structures that do not pack well together in bulk (in contrast to the regular packing of spheres). A bulk sample of carbon black has substantial void space; the larger and more complex the aggregate structure, the larger the internal voids in the bulk. Absorption of dibutyl phthalate into a carbon black sample measures the void space; the greater the dibutyl phthalate absorption, the greater the voids and hence the larger the aggregates.

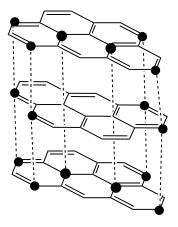
The dominant use of carbon blacks worldwide is in automotive applications, particularly tires. Carbon blacks improve the tensile strength of natural rubber by 40%, and of styrene-butadiene rubber (a major component of tires) by an order of magnitude. At a given amount of addition of carbon black into rubber, the smaller the particle size of the carbon black, the greater is the total interfacial area between the carbon black and the rubber. This provides increased tensile strength and increased resistance to tearing. The greater the "structure" – which in this application means the irregularity of the aggregate [F] – the more stiffness it imparts to the rubber. Carbon black stiffens rubber by replacing chains of deformable polymeric material with small, rigid particles that do not deform easily. As a result, the rubber product becomes less elastic. Then, when or if the rubber does begin to fail, the pathway through which the break or tear proceeds moves toward the carbon black aggregates. The more of these aggregates in the rubber, the longer is the total pathway that has to be opened up for a major tear or break to occur. Thus, the greater the carbon black loading, the higher the tensile strength. However, this is true only up to a point, typically around a carbon black loading of 30 volume percent. With even more carbon black, so much carbon black is in the mixture that it is difficult for the polymeric chains of rubber to wet all of the carbon black surfaces that are available. Carbon black added to rubber increases the breaking strength, but shortens the amount of extension at the point of rupture. In a sense, the interactions between individual rubber molecules are replaced by rubber-carbon black-rubber interactions.

A secondary application of carbon blacks is as pigments in making toners, printing inks, and plastics. A characteristic parameter is the blackness index [G], which is inversely proportional to particle diameter. Carbon black is also an excellent absorber of ultraviolet (UV) light. Because of this, carbon black additives find use in polymers to prevent UV degradation. Aside from absorbing some of the UV light, preventing it from being absorbed by the polymer instead, if the UV does initiate radical degradation processes in the polymer, carbon black can serve to terminate radical chain reactions.

## 24.4 Graphites

## 24.4.1 Natural graphite

Graphite occurs naturally in many parts of the world, including Siberia, Mexico, Madagascar, Sri Lanka, Quebec and Ontario in Canada, and New York state in the U.S. It represents the ultimate end product of catagenesis along the carbon-rich side of the hydrogen redistribution diagram. Accordingly, it tends to be found in sediments that have experienced a high degree of metamorphosis, for example, those



**Figure 24.5.** A portion of the graphite structure. The atoms identified with black dots are vertically aligned, as indicated by the dashed lines. The distance between planes is 0.3354 nm.

altered by contact with magmas. Tectonic stresses in the surrounding rocks might also have a role in formation of graphite.

Graphite has a highly anisotropic structure, see Figure 24.5. Within a plane, the carbon atoms participate in strong  $sp^2$  bonding. Between planes, relatively weak electrostatic interactions provide the bonding from one plane to another. Consequently, when graphite experiences a shear force in the direction of the planes, they slide easily. This gives natural graphite one of its major applications, as a lubricant. Powdered graphite makes a superb lubricant for high-temperature applications, where organic materials would vaporize or char and lose lubricity. Most metals would melt from overheating before graphite would be affected. Graphite also works well as a low-temperature lubricant, when the viscosities of organic liquids would be too high to allow parts to slide.

The anisotropic strength of graphite in response to shear is also responsible for the ability of graphite to leave marks when slid across paper or parchment. Graphite has been used for writing since ancient times; it is the "lead" [H] in the wooden pencils used by generations of schoolchildren. Other commercial applications of natural graphite include manufacture of crucibles and of electrodes for batteries.

## 24.4.2 Graphitization processes

The Acheson process [I] for making synthetic graphite was discovered in the 1890s. At that time, silicon carbide, also called carborundum, had been developed as an abrasive and a refractory material, and was manufactured in high-temperature electric furnaces. The reaction for silicon carbide synthesis is straightforward:

$$SiO_2 + 3C \rightarrow SiC + 2CO.$$

For this reaction, sand serves as the source of silicon dioxide; anthracite is used as the carbon source. Carbon monoxide is allowed to catch fire and burn as it leaks out between the bricks of the furnace walls. A carborundum furnace of the 1890s in full operation must have been quite a sight to behold. Acheson's key discovery, which may

have been accidental, was that allowing a furnace to get too hot resulted in production of graphite instead of carborundum, possibly via the reaction

$$\text{SiC} \rightarrow \text{C} + \text{Si}^{\uparrow}$$

Accidental or not, this discovery laid the foundations of the synthetic graphite industry. Nowadays petroleum coke is the preferred carbon source for probably 99% of the world's synthetic graphite, though anthracite certainly can serve as a raw material for production of some grades of graphite.

In its broadest sense, graphitization converts a carbon feedstock, such as petroleum coke or anthracite, into the well-ordered structure of graphite. Graphitization requires extreme temperatures, in the vicinity of 3000 °C. During production of artifacts of graphite, discussed below, materials engineers can manipulate the processes of forming the artifact (e.g. by molding, pressing, or extruding) and the graphitization reaction itself to obtain products in which the size of individual graphite crystallites and their orientation help establish the desired macroscopic properties. Because of this, synthetic graphites are sometimes called engineered graphites.

As the raw material experiences heat-up to graphitization temperatures, heteroatoms and hydrogen begin to be driven off, starting at around 1300 °C. Once temperature exceeds 1800 °C, turbostratic carbon begins to align and to start forming the graphitic structure. Above 2000 °C, the heteroatoms and most or all of the hydrogen have been driven off. Alignment of turbostratic carbon continues; the rate of alignment increases as temperature passes 2200 °C. Development of a fully graphitic structure is usually complete by 3000 °C. Formation of graphite occurs at temperatures >2500 °C, but with a trade-off between time and temperature. It may be possible to graphitize a specimen fully in an hour at 3000 °C, but many hours, possibly days, would be needed at 2500 °C.

Graphitization can be catalyzed by metals or metal oxides. These species react with carbon in disordered or non-graphitic structures, presumably because such carbon is not so thermodynamically stable as graphite. The carbides produced in this way decompose at higher temperatures into graphitic carbon, as Acheson discovered over a century ago. Quartz naturally present in anthracites appears to facilitate graphitization in exactly this way. Using the symbols ng and g to represent non-graphitic carbon, respectively, the reactions are

$$\operatorname{SiO}_2 + 3\operatorname{C}(ng) \rightarrow \operatorname{SiC} + 2\operatorname{CO}^{\uparrow},$$
  
 $\operatorname{SiC} \rightarrow \operatorname{C}(g) + \operatorname{Si}^{\uparrow}.$ 

Other treatments that preferentially react with disordered, non-graphitic carbon could also accelerate graphitization. Heat-treatment in a mildly oxidizing atmosphere is an example.

## 24.4.3 Electrodes

The dominant application of graphite electrodes is in arc furnaces for steelmaking. The use of graphite electrodes in this application is an extraordinary triumph of carbon material science. Graphite electrodes can be 75 to 750 mm diameter and up to 3 m long. At the tip where the electrical arc is struck, the temperature may reach  $3500 \,^{\circ}$ C. In the furnace bath of molten steel and slag, the temperature is  $1500-2000 \,^{\circ}$ C. But at the other end, some few meters away, the temperature is close to ambient. The carbon maintains

a temperature differential of perhaps 2000 °C over a distance of a few meters. The electrode is clamped at the top, and must maintain sufficient mechanical strength to support its own weight while sustaining this temperature difference. The electrode has to resist splitting due to thermal shock. The coefficient of thermal expansion must be low enough that the hot electrode will not expand to a point at which it cannot be withdrawn through the roof of the furnace. And, when the white-hot electrodes are pulled from the furnace, they must withstand oxidation by exposure to air, to say nothing of resisting catching fire.

Production of graphite electrodes relies on two principal ingredients, a filler and a binder. The filler is usually needle coke from delayed coking of petroleum products (Chapter 16). The binder is usually coal tar pitch, i.e. the residue from distillation of coal tar from by-product coke ovens (Chapter 23). Crushed and milled filler is mixed with binder at a temperature somewhat above the softening point of the binder. Most coal tar pitches are so viscous as to appear solid at room temperature; they tend to soften at temperatures of  $\approx 110 \,^{\circ}$ C, and have viscosities low enough to be workable about 20–40 °C above the softening point. The temperature of mixing is chosen to assure good wetting of the filler particles by the binder, but usually is below 160 °C. The amount of binder used depends to some extent on the particle size of the filler, and on the eventual use to which the manufactured item will be put. The range is large, from a binder:filler ratio of about 0.25 up to about 0.7 on a mass basis. The resulting mixture of binder with filler is called the green mix.

Subsequently, the green mix is extruded into a body (if intended for electrode manufacture, it looks like a large, black log) that is close to the dimensions desired in the final product. A large electrode could be 3 m long and 0.7 m in diameter. The extrusion temperature is below the mixing temperature, typically  $\approx 125$  °C. If the eventual product is not an electrode, the mix could instead be molded to a desired final shape. Molding is used, for example, in making graphite crucibles. Needle coke is highly anisotropic. In extrusion, the "needles" align parallel to the direction of the extrusion; in molding, they align perpendicular to the direction of the applied force.

The green carbon object is baked at about 800 °C. Green electrodes are placed inside stainless steel containers and surrounded (to fill the container) by a mixture of sand and metallurgical coke. The can-like stainless steel containers are called saggers, and the sand–coke mixture, the bake pack. If the density of the baked rod is low, suggesting that it contains voids or open pores, it is impregnated with petroleum pitch in vacuum at about 300 °C and then re-baked. In some cases, several cycles of impregnation and re-baking are applied.

When the baked rod is ready for graphitization, it is heated to  $\approx$ 3000 °C. Figure 24.6 illustrates the overall process.

Such temperatures can be achieved by electrical resistance heating. Two methods are used. In longitudinal graphitization, electrodes are placed in a furnace end-to-end. Current flows parallel to the direction in which the electrodes lie. Complete graphitization requires about six days. Graphitization is a batch process, the furnace being loaded with baked rods, the rods graphitized, and then the furnace being unloaded. The alternative, Acheson graphitization, also uses resistance heating, but the current flows perpendicularly to the long axis of the electrodes. In Acheson furnaces, the electrodes are packed in a so-called graphitizer pack, metallurgical coke sometimes mixed with

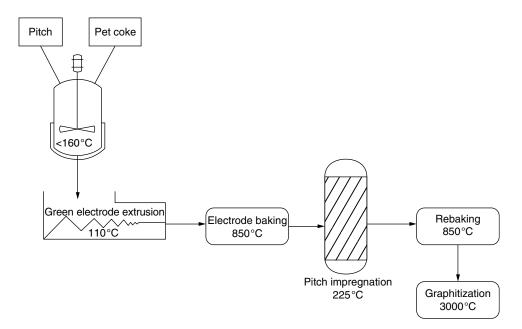


Figure 24.6. Process flow for production of graphite electrodes.

sand and sawdust, which provides insulation, but also some radiative heat transfer to the electrodes. Acheson graphitization can require 28 days per batch.

### 24.4.4 High-density isotropic graphites

Usually graphite is the exemplar of an anisotropic material, with strong covalent bonds within the planes of carbon atoms and weak electrostatic interactions between planes. The notion of isotropic graphite seems like an oxymoron, but the term applies to a material in which the individual crystallites of graphite are oriented in random directions. This material differs from the graphites in which extrusion or molding is intended to align the needle coke particles. The anisotropic ratio is the ratio of electrical resistivities parallel and perpendicular to the direction of extruding or molding. For an isotropic graphite, this ratio has values of 0.9-1.1. For the material also to be called high-density, its density must be >1.8 g/cm<sup>3</sup>, above the range (1.5–1.8) for conventional synthetic graphites.

High-density isotropic graphites can be produced by the same general procedure as for electrode graphites, with two changes. Filler particles are milled to very fine particle size, to help ensure a random orientation of particles as they undergo mixing with the binder. Second, molding is done in an isostatic press, to avoid preferential alignment created by unidirectional molding pressures. These isotropic graphites have valuable commercial uses, though the entire isotropic market today is only a small fraction of the electrode market.

High-density isotropic graphites are used to make heaters and crucibles in manufacturing single crystals of silicon for the semiconductor industry. This type of graphite is also used to make electrical discharge machining (EDM) electrodes. EDM offers a way to produce complex shapes to very tight tolerances, even in metals or alloys whose hardness or strength would make them extremely difficult to machine with conventional tools such as lathes and drills.

Nuclear graphites fall in the category of high-density isotropic graphites. Graphite has been used as a moderator (a substance to reduce the kinetic energy of neutrons produced from fission to a point at which they are capable of inducing another fission event) since the very first, hand-built nuclear reactor in 1942. Graphite has applications as the core material in some of the new-generation reactors, including the high-temperature gas-cooled reactors under development, and to help fabricate the fuel "pebbles" (which are actually about as big as tennis balls) for the pebble-bed nuclear reactor. In these applications, anisotropic thermal expansion could create stresses leading to failure. Therefore, a highly isotropic grade of graphite is desired for nuclear applications [J]. It remains to be seen whether the nuclear industry will revive from the coma induced by the Three Mile Island and Chernobyl accidents, but if it does, isotropic graphites could become a big business.

## Notes

- [A] Charles Martin Hall (1863–1914) was an American chemist who developed the electrolytic process through experiments done in a woodshed behind his home. Everywhere in the English-speaking world except in the United States, the element Al is called *aluminium*. In the U.S. it is *aluminum*. According to legend, Hall is personally responsible for this difference, because he accidentally misspelled aluminium in an advertisement promoting his process. Paul Héroult (coincidentally also 1863–1914) was a French scientist and highly skilled billiards player, whose work ran parallel to Hall's. Héroult's second-most important invention was the electric arc furnace for steelmaking, itself having challenging requirements for carbon materials. The successful commercialization of the Hall–Héroult process is said to have reduced the price of aluminum by a factor of 200.
- [B] Two black raw materials are not going to mix to produce a substance that is green. In this context, the word *green* has one of its less common meanings, i.e. unfired or untreated. This meaning derives from the early pottery and brick industries.
- [C] The long baking time represents a severe quality-control challenge for the aluminum industry. Nobody will know whether the anode is acceptable, or has cracked, fallen apart, or become otherwise unusable, until it emerges from baking. But, the mix that was used to make the anode was prepared three weeks earlier. If there were problems in formulating the mix that result in a poor anode, they won't be caught for three weeks. In the meantime, it is possible that more and more of the substandard mix has been formulated and molded into green anodes. There is a need for continuous development of test methods that allow predicting, accurately, the quality of a baked anode from a green mix.
- [D] Almost all pyrolysis reactions are endothermic, because they involve the breaking of bonds in stable compounds. However, acetylene is unusual in having an endothermic heat of formation (+227 kJ/mol). Other compounds having endothermic heats of formation include ethylene, carbon disulfide, hydrazine, and hydrogen cyanide.

- [E] To think of the structure of graphite, envision a new deck of playing cards. Each of the neatly stacked cards represents a layer plane of hexagonal  $sp^2$  carbon atoms, the planes being flat and aligned vertically with well-defined layer spacing. In a turbostratic carbon, some, indeed many, of these "planes" are actually folded, bent, or crumpled up. The alignment from one "plane" to another may also be twisted. A turbostratic carbon would be the same playing cards after long, hard use, and not carefully piled up.
- [F] In the carbon black business, the word *structure* refers to the structure of the aggregates, i.e. how big they are and what shape they take. The arrangement of atoms, layers of aromatic structures, and orientation of crystallites within one individual carbon black particle is usually called *microstructure*.
- [G] The blackness index is measured spectrophotometrically. Remarkably, it is possible to discern about 250 different shades of blackness, at least for a person with a well-trained eye and very good vision. The ability to discriminate between this many shades of black varies from person to person, and on how well the black coloration was done.
- [H] The confusion in names, specifically why graphite is sometimes called "lead," dates from the sixteenth century, when a deposit of graphite was discovered in England. Because of its grayish-black metallic appearance, the graphite was given the name *plumbago*, variously translated as lead ore, or black lead. Presumably, the graphite was taken to be a form of lead, for which the Latin name is *plumbum*. The difference should be instantly obvious to anyone who has held a piece of graphite in one hand and an equal-sized piece of lead in the other, since lead is more dense by a factor of five (11.3 vs. 2.2 g/cm<sup>3</sup>, respectively). The leadworts, a family of decorative plants, are also known as plumbagos.
- [I] Named for the American chemist Edward Acheson (1856–1931). Acheson's first foray into carbon materials science came when he worked for Thomas Edison, developing carbon materials for filaments in incandescent lighting. Later, he developed methods for making cubic zirconia (ZrO<sub>2</sub>), still sold as "artificial diamonds," and for silicon carbide. The latter product, sold under the name carborundum, finds extensive use as an abrasive and as a refractory.
- [J] The 1957 accident at the Windscale reactor (now Sellafield) in England has sometimes been attributed to anisotropic graphite in the moderator expanding to a point where it was exposed to air and caught fire. However, it was actually fuel cartridges that caught fire, not the graphite.

#### **Recommended reading**

- Delhaès, P. *Graphite and Precursors*. Gordon and Beach: Amsterdam, 2001. A collection of chapters by various authors that includes much useful background on the fundamentals of graphite chemistry and physics, and on graphite technology.
- Donnet, J.B., Bansal, R.C., and Wang, M.J. *Carbon Black*. Taylor and Francis: Boca Raton, FL, 1993. Again an edited collection of chapters by various experts, providing a survey of carbon black production and uses.
- Marsh, H., Heintz, E.A., and Rodríguez-Reinoso, F. Introduction to Carbon Technologies. Publicaciones de la Universidad de Alicante: Alicante, Spain, 1997; and Marsh, H. and Rodríguez-Reinoso, F. Sciences of Carbon Materials. Publicaciones de la Universidad

de Alicante: Alicante, Spain, 2000. These two companion volumes each represent collected chapters prepared by authors working in various fields of carbon technology or science. Taken together, these books provide a very thorough grounding in carbon materials.

- Pierson, Hugh O. Handbook of Carbon, Graphite, Diamond, and Fullerenes. Noyes Publications: Park Ridge, NJ, 1993. A useful introduction to carbon materials. Many parts of this book are relevant to the present chapter, along with topics not included here, such as carbon fibers and diamonds.
- Song, C., Schobert, H.H., and Andrésen, J.M. *Premium Carbon Products and Organic Chemicals from Coal. Report No. CCC/98*, International Energy Agency: London, 2005. This report focuses only on coal as a feedstock, but discusses graphites, activated carbons, and other products relevant to this chapter. A useful survey of the field up to its time of publication.

Evidence that Earth is heating is incontrovertible. Glaciers and permafrost are melting. Sea level is rising. Deserts are spreading. Growing seasons are getting longer in far northern latitudes. Migratory species arrive at their summer breeding grounds earlier and remain later. Animals, including some of the less-pleasant snakes and diseasecarrying insects, are increasing their ranges. Meteorological records show that the past decade has been the warmest on record. So many independent observations from different areas of science make an exceptionally strong case that a real effect is occurring.

Like any other system, temperatures on Earth are governed by a simple heat balance:

(Heat in) - (Heat out) = (Heat retained in system).

Several sources provide heat. These include incoming solar radiation, heat generated by human activity, and heat from decay of radioactive species in the Earth's interior. Of these, solar radiation dominates, by far. It is estimated that the entire yearly energy needs of all of humankind could be met by capturing and converting all of the solar energy falling on Earth for about 45 minutes. Heat is lost primarily by radiative heat transfer back into space, much in the infrared. The balance between heat coming in, mainly solar energy, and heat going out, mainly infrared radiation to space, maintains the average global temperature. Any change in either term necessarily results in a change in the amount of heat retained, which in turn eventuates in a change in average global temperature. Because temperature has a major role in affecting climate, the net effect is a change in global climate.

This observation that Earth is warming has not been linked to evidence of a steady rise in energy production in the sun, nor to significant increases in solar energy reaching Earth. The "Heat in" term in the heat balance equation has not changed significantly. Because of the abundant evidence that the "Heat retained in system" term is increasing, the cause must be that the amount of heat being lost to space ("Heat out") has been decreasing.

At the temperatures we experience on Earth, radiative heat transfer occurs mainly in the infrared. Some components of the atmosphere can absorb infrared radiation. These include methane, carbon dioxide, water vapor, nitrous oxide, and chlorofluorocarbons. When the concentration of any of these gases increases in the atmosphere, so does the amount of infrared radiation absorbed. A molecule absorbing infrared radiation is promoted to a higher energy state. Eventually the molecule relaxes to its ground state and releases the absorbed energy. The released energy can be emitted in all directions; inevitably some is re-radiated back to Earth. Heat back into space is reduced. This increases the amount of heat retained, leading to an increase in average global temperature. An analogy suggests that infrared-absorbing gases in the atmosphere retard heat loss in the same way that the glass panels in the walls and roof of a greenhouse act to keep heat inside [A]. For this reason, the infrared-absorbing gases are collectively known as greenhouse gases. The warming being experienced on Earth as a result of increased atmospheric concentrations of greenhouse gases is popularly known as the greenhouse effect, though better referred to as global warming or global climate change.

Even in the complete absence of human activity, or indeed complete absence of humans, the atmosphere would still contain greenhouse gases. Carbon dioxide, for example, comes from decay of organic matter, from volcanic eruptions, and from natural forest or prairie fires. Because some amount of greenhouse gases occurs naturally, Earth is warmer than it would have been if they were not present at all in the atmosphere. If there were no greenhouse gases whatsoever, Earth's average temperature would be about -5 °C. This difference in temperature between -5 °C without greenhouse gases and the global mean of about 14 °C represents the natural greenhouse effect. Without it, life would be much different [B].

Human activities add to the concentration of greenhouse gases in the atmosphere. This increase in greenhouse gas concentration brings its own contribution to the warming of the planet. The additional warming, over and above the natural greenhouse effect, is known as the anthropogenic greenhouse effect, the term chosen to call attention to the role of human activity. Examples of human activities include leaks of methane from natural gas systems, conversion of limestone to lime in the cement industry, and burning forests to create additional cropland. One activity among these many others that generates substantial greenhouse gas emissions, as carbon dioxide, is the burning of fuels that contain carbon, which in fact is the largest source of anthropogenic  $CO_2$  emissions.

Because  $CO_2$  emissions link directly to fuel use, carbon dioxide is the focus of this chapter. But, three facts should be kept in mind: first, carbon dioxide is not the only greenhouse gas. Second, anthropogenic emissions are not the only source of atmospheric carbon dioxide. And, third, fossil fuel combustion is not the only source of anthropogenic emissions.

Without doubt, the most important and effective approach to reducing carbon dioxide emissions in the near term lies in energy conservation. A doubling of the fuel economy of the vehicle fleet would allow everyone to drive just as much as presently, but consuming half the fuel and emitting half the  $CO_2$ . In the long term, the solution to reducing or eliminating  $CO_2$  emissions is to increase reliance on energy sources that do not contain carbon. These include solar and wind energy, hydrogen (if it did not come from steam reforming or gasification of a carbon-containing feedstock), and nuclear energy. Some sincere persons argue that humans must stop using carbon-based fuels, especially fossil fuels, immediately. That will not happen. The world lacks the financial wherewithal and the manufacturing capacity to replace, on any time scale short of multiple decades, all of the electric generating stations, vehicles, process heaters, metallurgical smelters, and domestic appliances that rely on carbon-based fuels.

Biomass offers a potential alternative to fossil fuels, retaining the practical advantage of being usable in the same devices that utilize fossil fuels, often with little or no modification to the hardware. Biomass (Chapters 4–6) represents a short-circuit of the global carbon cycle, in the sense that the carbon dioxide emissions from biomass

utilization are in principle removed from the atmosphere in the next growing season, when the next-generation crops are grown. However, some uncompensated  $CO_2$  emissions come from fossil fuels used in agricultural machinery, in transport of harvested biomass to processing plants, and in conversion of biomass to products such as biodiesel and ethanol. For some forms of biomass, such as starch-based ethanol, the food vs. fuel argument remains unresolved. Long-term soil productivity under intense monoculture cultivation also remains an issue, as does the availability of water resources for growing the biomass. But, these concerns aside, biomass seems set to continue to increase in importance as an energy source, though it is questionable whether the world can grow enough biomass to provide the equivalent amount of energy obtained from fossil fuels.

The world will continue to rely on fossil fuels for decades to come. The question that must be confronted is how to deal with greenhouse gas emissions, and especially carbon dioxide, from fossil fuel utilization. Broad strategies go back to the global carbon cycle (Chapter 1) and identification of sources and sinks. It might be hoped that someday the world's nations will agree on, and implement, practical solutions to stopping destruction of such important sinks as the rain forests, and even to begin to restore the biosphere's capacity for taking up carbon dioxide. Though such endeavors lie well outside the realm of fuel science and engineering, this field can focus on the issue of sources.

It cannot be over-emphasized that the most effective practical approach to reducing carbon dioxide emissions lies in energy conservation and increased efficiency of energy use. Even so, state-of-the-art energy-efficient utilization of fossil fuels still produces some  $CO_2$ . The next step becomes that of finding ways to deal with the  $CO_2$ , to prevent its getting into the atmosphere. The approaches for doing this are called carbon management, or carbon capture and storage (CCS). Increased worldwide concern about global warming has led to development of many tactics for CCS. Some have looked very attractive in small-scale trials and are beginning to move into commercial application. Others derive from some uncharted realm of thought that lies well past absurd. The sections that follow discuss some CCS methods that seem to offer promise. Some are already in large-scale use, some are being tried; some are in development. Much excellent science and engineering has been, and must continue to be, devoted to CCS.

# 25.1 Carbon capture and storage

#### 25.1.1 Algae

Photosynthesis is a major pathway for removing carbon dioxide from the atmosphere. Growth of green plants provides a  $CO_2$  sink in the global carbon cycle. Because of that, it can be useful to grow plants deliberately for the primary purpose of capturing  $CO_2$ . Many plants could be candidates for this application. Ideally, these should grow very rapidly, to provide high rates of  $CO_2$  uptake. It would be useful if they could be grown near major  $CO_2$  sources, even co-located with the source. An additional bonus could be obtained if the plants, once grown, could be harvested for some useful purpose, such as conversion to biofuels. Algae fulfill these criteria.

Algae exist as four distinct classes: *Bacillariophyceae*, the diatoms; *Chlorophyceae*, the green algae; *Chrysophyceae*, the golden algae; and *Cyanophyceae*, blue-green algae. Each class has several genera; at the species level, there are over a hundred thousand species of algae. Diatoms are unicellular organisms that sometimes form colonies with organized structures, such as filaments. Diatoms encase themselves in silica. When they die, the silica shells accumulate to form diatomaceous earth, which finds use in chemical processes as a filter aid, and readily absorbs nitroglycerine to produce dynamite. The green algae, ancestors of today's higher plants, encompass several thousand species. Sea lettuce (*Ulva lactuca*), a green "slime" sometimes found on rocks in tide pools, is a green alga. Blue-green algae have an important role in Earth history. Their production of oxygen as the by-product of photosynthesis may have been the contributing factor that converted Earth's primitive reducing atmosphere into an oxidizing atmosphere, fostering subsequent evolution of aerobic organisms.

Utilization of carbon dioxide by algae follows the reactions described in Chapters 3 and 5. Photosynthesis converts carbon dioxide to glucose; subsequent reactions utilize the glucose to synthesize lipids. It appears that enhanced  $CO_2$  concentrations increase the rate of growth, so that at least some algae not only tolerate, but even thrive on, concentrations of  $CO_2$  two to three orders of magnitude higher than currently in the atmosphere. A few species can even tolerate a 100%  $CO_2$  atmosphere.

A second benefit could be achieved if the algae had not only high growth rates, but also produced high concentrations of lipids. In higher plants, only a small fraction of the total plant material contains significant amounts of lipids. This is not the case with algae. The algal lipids could be extracted and used for biofuel production. Biofuel would represent an additional revenue source for a fuel processing or conversion facility. If the algal biofuel were blended with liquids derived from, e.g., Fischer– Tropsch liquids from coal, possibly some benefit might be gained by counting the renewable or "green" contribution to the total liquid product. The residue after extracting the oil could be considered a possible feed to a gasifier or combustor.

In favorable conditions, algae grow readily in open ponds. This can be observed in, for example, farm ponds in the summertime, when the surface of the pond might be covered completely with a green layer of "pond scum" algae. Artificial ponds could be created, in which algae can be encouraged to grow and absorb carbon dioxide. Because  $CO_2$  uptake would be almost entirely at the surface, large areas are required to achieve significant  $CO_2$  utilization. An improved approach would make use of reaction in a volume, rather than at a surface. This can be achieved by carrying out the photosynthesis in transparent reaction vessels, photobioreactors. Figure 25.1 provides an example.

In these reactors, a suspension of algae in an aqueous nutrient medium is sparged with  $CO_2$  to obtain good contact of  $CO_2$  with algae cells. The continuous flow of  $CO_2$ through the reactor should keep the contents mixed without relying on stirrers or agitators. As the total mass of algae increases, they reduce the light intensity in the reactor, so provision must be made for their periodic harvesting. The need to achieve effective light intensities throughout the entire cross-section of the reactor limits diameters to  $\approx 0.4$  m.

Algae used in  $CO_2$  capture must fulfill several criteria. The algae should be capable of high growth rates and high lipid production. Buoyancy of the algal cells is important in photobioreactor operation, so that the cells do not settle out and coat the walls of a



**Figure 25.1** A photobioreactor using algae to capture carbon dioxide. This configuration of reactor is called a biofence, because the configuration of the tubes containing algae resembles a fence.

bioreactor, somewhat like the green growth that can form on the sides of a home aquarium. The algal cells eventually need to be recovered from the bioreactor, by a simple and inexpensive process. Flocculation would aid in their separation; such processes could be an auto-flocculation mechanism, or induced by, e.g., changes in the pH of the medium. Of the many thousands of candidate algae species, it appears that those in the genus *Nannochloropsis* meet most of these criteria reasonably well. In the most favorable cases, some algae contain  $\approx 40\%$  lipids. Among marine algae, lipid content relates inversely to the growth rate, i.e. those with rapid growth have a low percentage of lipids in their accumulated weight. The *Nannochloropsis* species offer the best balance between growth rates and lipid contents.

## 25.1.2 Biochar

Pyrolysis of fossil or biofuels (e.g. Chapter 6) is invariably accompanied by char formation. In some cases, this is the point of running the process – production of charcoal being an example. However, if pyrolysis were being done to make gaseous or liquid fuels, and no ready market existed for the char, it would be possible simply to bury the char. Doing so would sequester carbon in amount equivalent to the char yield from the process. Some temporary carbon sequestration can be accomplished by burying, or plowing under, crop residues or compost. In the terminology of soil science, the carbon in such materials is labile, in that it will convert to carbon dioxide and escape to the atmosphere in a few years. In comparison, carbon in char is said to be stable, in that it could remain in the soil for centuries or millennia.

Deliberate pyrolysis of biomass to produce char for carbon sequestration has multiple benefits in addition simply to locking up carbon. The product has several names, but is commonly called biochar or Agri-char, sometimes *terra preta* (dark earth) [C]. Trials of biochar in Australia have produced a doubling or, in a few cases, tripling of crop production when biochar is added to soil at dosages of 10 tonnes per hectare. Several factors contribute to its beneficial action. The char is likely to retain some of the nitrogen, phosphorus, and potassium from the original plant matter. These elements are important plant nutrients and constituents of fertilizers. The action of groundwater or soil organisms on biochar could release them back to the soil, where they would be available to help stimulate growth of the next generation of plants. Biochars are very porous solids, readily taking up and holding moisture. Retention of water in the char also aids crop growth. By virtue of stimulating plant growth, biochar has a double impact on  $CO_2$ . First, its addition to the soil already sequesters carbon. Second, the increased growth of plants removes  $CO_2$  from the atmosphere because more photosynthesis is taking place.

Feedstocks for biochar production could be various forms of biomass. If biomass were to be grown specifically for biochar production, it is likely that fast-growing plants would be selected for this application. They could include switchgrass (*Panicum virgatum*) and hybrid poplars (genus *Populus*). Reactors could be externally heated kilns. Gases and bio-oil products represent potential additional revenue streams. The composition of the oil depends on the specific feedstock and on pyrolysis conditions. It seems reasonable to expect that the oil could be upgraded further into useful fuel or chemical products, not unlike the wood chemicals obtained from charcoal production. Other feedstocks could be municipal solid waste, or waste products from the food and forest products industries. Not much seems to be known about the benefits, if there are any, of burying the char from fossil fuel pyrolysis. Use of agricultural (crop) wastes is an attractive option. Annual production of agricultural waste worldwide amounts to some four gigatonnes. A pyrolysis process that yielded only ten percent biochar could produce enough to fertilize some forty million hectares of arable land, at the dosage rate used in Australia.

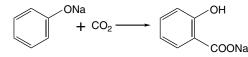
Commercialization of biochar production could take two directions. One would be production in large, centralized facilities. If so, biochar plants would face the same economic issue that ethanol and biodiesel plants also face: it is not economical to collect and ship biomass from beyond a certain radius from the centralized facility. The numerical value of this radius depends on the economic assumptions used, but ranges from a pessimistic 20 km to an optimistic 160 km. A radius of 50–80 km seems reasonable. The alternative is biochar production in very small, decentralized facilities. Kilns are mature, indeed ancient, technology. Biomass pyrolysis would be "low tech." Farmers could build and install their own biochar units. Alternatively, a biochar kiln could be mounted on the back of a truck and taken from farm to farm as needed. And, a comprehensive biofuel program could involve harvesting and shipping biomass to a centralized ethanol or biodiesel plant within the economically limiting radius, and beyond that distance converting biomass to biochar in small, decentralized units.

An additional benefit of biochar comes from its ability to displace some of the nitrogen-based fertilizer needs for fields where biochar is used. Many fertilizers are either produced from fossil fuels, or consume fossil fuels during processing. Reduced fertilizer demand may impact  $CO_2$  emissions from the production facility. More importantly, nitrogen fertilizers represent a major source of nitrous oxide emissions. Nitrous oxide is a greenhouse gas, about 270 times better at absorbing infrared radiation than is  $CO_2$ . Reducing  $N_2O$  emissions by using less nitrogen-based fertilizer should have its own impact on global climate change. The over-use of nitrogen-based fertilizers also contributes to water pollution, as nitrates or other nitrogen compounds migrate into natural bodies of water.

### 25.1.3 Chemical uses of CO<sub>2</sub>

The world's chemical industry uses about 120 Mt of carbon dioxide per year. The largest use is in synthesis of urea, discussed below. Other major processes using carbon dioxide are production of salicylic acid, methanol, and various organic carbonates, including poly(propylene carbonate).

The key compound in the synthesis of aspirin, salicylic acid (*o*-hydroxybenzoic acid), is prepared from phenol by the Kolbe–Schmitt reaction:



Production of aspirin in the United States alone is over 20 000 tonnes per year, a rate roughly equivalent to every man, woman, and child taking one tablet a day, every day! [1].

The Kolbe–Schmitt reaction converts phenol to *ortho-* or *para-*hydroxybenzoic acid. The reaction proceeds via formation of the sodium or potassium salt of the phenol, followed by reaction with carbon dioxide. In the original synthesis, from the 1870s, the sodium salt was heated with carbon dioxide at 180-200 °C under elevated pressure. Whether sodium or potassium is used to form the phenoxide has an important effect on the outcome of the reaction. Sodium phenoxide gives high yields of salicylic acid, whereas the potassium salt favors the *para-* isomer.

Organic carbonates are useful as solvents and as intermediates in various syntheses. They also have potential as fuel additives. Several routes exploiting carbon dioxide are available for synthesis of organic carbonates, of which the most straightforward reacts carbon dioxide with an alcohol, e.g.

$$2 \operatorname{ROH} + \operatorname{CO}_2 \rightarrow (\operatorname{RO})_2 \operatorname{CO} + \operatorname{H}_2 \operatorname{O},$$

typically at 140–190 °C. Reaction of alcohols with urea represents another potential route to carbonates:

$$2 \text{ ROH} + \text{H}_2\text{NC}(\text{O})\text{NH}_2 \rightarrow 2 \text{ NH}_3 + \text{ROC}(\text{O})\text{OR},$$
  
 $2 \text{ NH}_3 + \text{CO}_2 \rightarrow \text{H}_2\text{NC}(\text{O})\text{NH}_2 + \text{H}_2\text{O}.$ 

Ammonia is recycled to produce urea by reaction with  $CO_2$ , so the net process corresponds to synthesis of organic carbonates from alcohols and  $CO_2$ .

Dimethyl carbonate is a potential organic solvent, octane booster, and intermediate in other reactions, with potential for a large and growing market in the future. The direct route to this compound involves reaction with methanol:

$$2 \text{ CH}_3\text{OH} + \text{CO}_2 \rightarrow (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O}.$$

An alternative route uses urea and methanol, of interest because both feedstocks can themselves be made from carbon dioxide. The reaction represents the "methanolysis" of urea,

$$H_2NCONH_2 + 2 CH_3OH \rightarrow CH_3OC(O)OCH_3 + 2 NH_3.$$

In this process, ammonia could be captured and recycled to urea synthesis; if that were done, then the net reaction is

$$CO_2 + 2 CH_3OH \rightarrow CH_3OC(O)OCH_3 + H_2O.$$

Polycarbonate resins are strong, transparent materials often used as substitutes for glass (e.g. as lenses in eyeglasses). Capturing the automobile glass market would not only add to safety of automobiles, but enhance demand for a product that could be made from  $CO_2$ . The dominant monomer in production of polycarbonates is diphenyl carbonate, normally made using the dangerous and toxic phosgene as an intermediate. Organic polycarbonates also have applications that include food packaging, foam-cast automotive parts, and electronics processing. Wide-scale production of poly(propylene carbonate) from propylene oxide and carbon dioxide would be desirable because it currently has several industrial uses in the areas of ceramic binders, adhesives and coatings. Production of polycarbonates from copolymerization of  $CO_2$  and epoxides represents a potentially less expensive and significantly "greener" route to these materials than do current commercial processes, which often involve phosgene.

#### 25.1.4 Coalbed methane recovery

Two processes produce methane during coal formation. Biogenic methane is produced by anaerobic bacterial degradation of organic matter during diagenesis. Additional methane is produced during catagenesis reactions in coalification (Chapter 8), sometimes being referred to as thermogenic methane. Methane becomes adsorbed in the pore system of the coal. Accumulated in this way, the gas is referred to as coalbed methane (CBM). With petroleum and conventional natural gas, the fuel is generated from a source rock, then usually migrates through the crust until it accumulates in porous rock (the reservoir rock) capped by some impermeable rock formation that keeps the oil or gas in the reservoir. With CBM, coal is both the source rock and the reservoir rock. A methane-rich coal seam could contain six to eight times as much methane as the same volume of sandstone in a conventional natural gas reservoir.

CBM has both good and bad characteristics. On the negative side, methane is a hazard in mines. If it accumulates in a high-pressure pocket in the seam, this pressure can be released suddenly when the mechanical integrity of the coal fails. These so-called outbursts release high-pressure gas and blast coal and rock fragments into the mine tunnel, maiming or killing miners. Methane–air mixtures can be explosive, inadvertently

triggered by a spark or open flame. The first shock wave can create a cloud of coal dust in the tunnel, leading to a second, even more violent explosion of the dust–air mixture. The hazards of methane build-up in coal mines have been recognized for at least two centuries, yet every year miners die in gas explosions, especially in mining activities in countries with a cavalier or non-existent attitude toward mine safety [D]. Not only is methane a potentially lethal hazard in mines, it is also a potent greenhouse gas, absorbing about eleven times as much infrared as carbon dioxide, per molecule. Venting coal mines, or allowing methane to seep into the atmosphere, contributes to global climate change.

On the other hand, methane is an excellent fuel. Recovery of CBM provides a fuel resource while at the same time its removal from coal seams reduces risk to miners and keeps the gas from entering the atmosphere. CBM can be a significant fuel resource in countries that have coal reserves. In the United States, for example, CBM supplies about 10% of the total natural gas consumption.

An additional benefit accrues from injection of  $CO_2$  into a coal seam to stimulate production of methane.  $CO_2$  is more strongly adsorbed to coal surfaces than is methane.  $CO_2$  displaces adsorbed methane, and on average two  $CO_2$  molecules replace one of  $CH_4$ . As with any gas adsorption onto a solid, the amount of available surface area is very important. The extent of pores, fractures, and cleats in the seam affects how easily the  $CO_2$  can move through the seam, and the  $CH_4$  move out. There may be shrinkage or swelling, or both, of the coal as one gas displaces the other. Water might form aqueous solutions of  $CO_2$  that would have behavior very different from that of gaseous  $CO_2$ .

The best coal seams for potential  $CO_2$  sequestration with CBM recovery would be those having high methane content but which cannot be mined by present technology. Once  $CO_2$  has been sequestered, that coal is off-limits for use until a time comes when we learn how to use a  $CO_2$ -saturated coal without releasing all the sequestered  $CO_2$ back to the atmosphere. Many factors can make a coal seam unmineable. One is extreme depth; the costs of creating and operating a mine to access the coal may be greater than the revenue from selling it. Regardless of depth, the seam may be too thin to be worth mining, or it may not extend continuously over an adequate area. Or, the coal may simply be of poor quality – too high a sulfur content, or too high an ash yield, as examples.

Like the use of injected  $CO_2$  in enhanced oil recovery, discussed below, where the oil is a desired and marketable product, with CBM the collected methane could also be sold. Revenue could help offset the cost of the  $CO_2$  sequestration. But, unlike the case with oil, many of the candidate seams for  $CO_2$  sequestration are at relatively low pressure and temperature, reducing the cost of the necessary  $CO_2$  compression. Assuming that a prime source of  $CO_2$  for CBM recovery would be from coal-fired power plants, often such plants are located very close to coal seams. This would reduce the need, and cost, for long-distance pipeline transport of  $CO_2$ .

#### 25.1.5 Enhanced oil recovery

Recovery of oil begins with relying on natural pressure in the reservoir to help force oil to the surface, a process known as primary recovery. As pressure begins to drop, more oil can be obtained by secondary recovery, which involves injecting water into the

reservoir to help push the oil to the surface. Depending on the quality of the oil and the local geology, primary and secondary recovery can extract 20-40% of the oil. This leaves a lot of oil still in the ground. (The average recovery of oil from the world's oilfields is about 35%.)

Tertiary oil recovery, also called enhanced oil recovery (EOR), can boost the percentage of oil recovered to the 30–60% range. The term enhanced oil recovery covers a range of technologies, collectively involving heating, gas injection, use of chemical additives, or use of microbes, to increase the amount of oil that can be recovered. While EOR is a generic term that encompasses many methods, one method – carbon dioxide injection – has particular interest because it confers the double benefit of increasing oil recovery and sequestering carbon dioxide at the same time. Currently most  $CO_2$  used in this application is separated from natural gas. Interest for future years would focus on  $CO_2$  from combustion or gasification sources. Injection for oil recovery can consume 0.3–1 t of  $CO_2$  per barrel of oil recovered.

Injected carbon dioxide can work in two ways. At depths less than  $\approx 0.5$  km, carbon dioxide does not mix with the oil. Its principal benefit seems to be pushing oil out ahead of it, as it expands from the high pressure at which it was injected. A second benefit is that the gaseous carbon dioxide is able to penetrate fine pores or fissures in reservoir rocks that are not accessible to water, and so contain oil that could not be forced out during secondary recovery with water. At greater depths, CO<sub>2</sub> becomes supercritical (critical constants are 31 °C and 7.4 MPa). Supercritical CO<sub>2</sub> mixes with oil, reducing viscosity and surface tension. These effects make it easier to release oil from the pores in the reservoir rocks, and make it easier for oil to flow to the wellbore. CO<sub>2</sub> injection pressures are  $\approx 12$  MPa. The overall success of EOR by CO<sub>2</sub> injection depends on the temperature, pressure, and chemical composition of the oil. This technique works best for oils of  $> 22^{\circ}$  API gravity, and viscosity <10 mPa·s. Recommended depths of injection depend on API gravity of the oil, but range from  $\approx 0.8$ –1.3 km.

Since supercritical CO<sub>2</sub> mixes with the oil, some of the CO<sub>2</sub>, half to two-thirds, returns to the surface with the oil. It is usually re-injected into the well, rather than being vented to the atmosphere. Around the world the sequestration capacity for CO<sub>2</sub> via EOR is estimated to be equivalent to about 125 years' production of CO<sub>2</sub> in fossilfuel fired power plants. But, two problems lurk in this optimistic picture. First, it is necessary to separate the CO<sub>2</sub> from flue gas, which could be costly, because flue gas contains only some 10–15% CO<sub>2</sub>. (This suggests that further work on direct use of flue gas in EOR would be worthwhile.) Second, the separated CO<sub>2</sub> has to be moved to the oilfields where it can be used. Fortunately, a continuously growing infrastructure is developing. The United States alone now has about 5000 km of CO<sub>2</sub> pipelines. This still involves compression and pumping costs.

#### 25.1.6 Mineral carbonation

Incorporating carbon dioxide into minerals in Earth's crust, forming carbonates, is one of the natural processes by which  $CO_2$  is removed from the atmosphere. Similar processes could be used as  $CO_2$ -capture technology, provided that the kinetics could be substantially improved. Such is the aim of the processes of mineral carbonation.

In principle, numerous minerals are candidates for carbonation. The first criterion is that the mineral has to be "carbonatable," i.e. should contain high concentrations of

elements known to form insoluble, stable carbonates. This is the key to locking up the  $CO_2$ . A second criterion is that the candidate mineral should exist in large quantities near Earth's surface, readily and inexpensively available by current mining techniques. This is the key to developing a commercially viable mineral carbonation CCS process. The near future is not likely to see commercialization of large-scale CCS processes relying on rare minerals or those requiring heroic mining endeavors, regardless of how stable the carbonates and how fast they form. While many elements form insoluble, stable carbonates, ones that also occur in large concentrations in accessible, relatively inexpensive minerals are limited to calcium, magnesium, iron, and manganese.

Regardless of the specific mineral, two strategies exist for carrying out carbonation. One involves reaction with carbon dioxide with the intent of forming carbonates by a direct gas-solid reaction, or in aqueous slurry. The other involves reaction in an aqueous medium in which some of the elements forming carbonates would leach from the mineral and form a carbonate by reaction in solution. Both have advantages and disadvantages, mainly associated with achieving acceptably high rates of carbonation. Direct reaction may be simpler in concept, but requires high-pressure and high-temperature operation for good reaction rates. The high-pressure, high-temperature system has high capital costs and is likely to have high operating and maintenance costs. The aqueous system would be less expensive to procure and operate, but requires a method of liberating the carbonate-forming elements from the mineral. Both processes require some combination of crushing, grinding, or other preparation operations to make the mineral ready for reaction.

Serpentine [E] provides an example of a feedstock for mineral carbonation. The reaction can be represented as

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 \downarrow + 2SiO_2 + 2H_2O.$$

Serpentine meets both criteria for a candidate mineral. It contains 29% magnesium, which forms a stable carbonate. MgCO<sub>3</sub> occurs in nature as the mineral magnesite; its solubility in water is  $\approx 0.1$  g/l. Commercially useful deposits of serpentine crisscross the globe, from New Zealand to Norway, from China across Europe and into the United States. The issue is to achieve acceptable carbonation kinetics. Various ways of disrupting the serpentine structure have been tried for making the magnesium readily accessible for reaction. These include grinding to extremely fine particle sizes to enhance the surface area-to-volume ratio, high-temperature heat-treatment (known as roasting in the mineral industries), or leaching with various acids.

Acid leaching mobilizes magnesium and other carbonate-forming elements into aqueous solution, where they could react with dissolved carbon dioxide. However, insoluble carbonates do not form at low pH. A low-pH leaching step needs to be accompanied by, or followed by, a pH adjustment to move the system into a high-pH realm where  $CO_2$  is readily soluble and carbonates precipitate. While this makes the flow sheet more complicated, overall it still offers a process likely to be less expensive than roasting followed by high-pressure direct carbonation.

Other minerals can also be considered as candidates for carbonation. Many basalt rocks contain about 10% calcium, 8% iron, and 7% magnesium. Olivine,  $Mg_2SiO_4$ , containing 34% magnesium, has attracted much interest as a prospective mineral feedstock. The total reserves of all the likely minerals for carbonation are so large that, in theory, they could easily sequester all of the carbon dioxide generated by burning all

of the fossil fuels remaining on Earth. (One way of looking at this is in terms of the composition of Earth's crust, which contains 2 mole percent magnesium, but only 0.04 mole percent carbon.)

Some industrial processes also make candidates for carbonation, usually as byproducts or wastes. In the iron industry, lime or limestone is commonly used in furnaces as a flux, to help produce a slag that takes up various impurities from the iron ore. Though the composition of this slag can vary greatly, it is essentially a calcium silicate, of  $\approx 40\%$  calcium. In many places such slags are either a waste, or sold as low-value by-products for, e.g., use as an aggregate in cement or asphalt for road construction. Iron slags, as well as other industrial products that contain significant amounts of calcium and magnesium, have potential use in mineral carbonation. In principle, a slag carbonation facility could be co-located with a steelmaking complex, so that some of the CO<sub>2</sub> emissions could be handled directly on-site.

Where better opportunities are lacking, the products of mineral carbonation could be buried, to lock up the carbon in the crust for millennia. However, many of the products have significant commercial potential. The material known as precipitated calcium carbonate (PCC), much more pure than natural sources of CaCO<sub>3</sub> such as limestone, finds high demand in the paper industry. PCC is used as a filler, to add "body" to the paper, and is desirable because it helps the paper receive and retain printing ink. Magnesium carbonate is valuable for making refractory bricks for the pyrometallurgical industry. Iron carbonate or hydrous oxide could be converted to magnetite,  $Fe_3O_4$ , in short supply as a heavy-media agent in coal cleaning (Chapter 18). If pH adjustment in an aqueous slurry process were done using ammonia, the possibility exists for recovering ammonium salts (e.g. ammonium sulfate) for sale to the fertilizer industry. Even the silica residue after reaction might have some value, depending on its surface area and composition. The oxymoronic "white carbon black," currently made from silicon tetrachloride, has numerous applications and, in its finest grades, can bring five US dollars per kilogram. Revenues from by-product sales could have significant impact on reducing the net cost of a mineral carbonation operation.

#### 25.1.7 Photocatalysis

Combustion is done because it is exothermic; the heat liberated is converted to mechanical work, used to raise steam, or to supply process or space heat. Carbon dioxide is the inevitable product. If we think of going in the opposite direction – converting carbon dioxide back to hydrocarbon fuels or chemicals – necessarily the process is endothermic. An energy source for this  $CO_2$  conversion should not itself produce yet more  $CO_2$ , and should be of very low cost, ideally free. Solar energy meets these criteria.

Solar energy could be used for carbon dioxide conversion in two ways. First, solar energy can be used to make hydrogen, either directly via photolytic splitting of water, or by generating photovoltaic (PV) electricity which is then used to electrolyze water. Chapter 21 discussed synthesis of methanol from  $CO_2$ , i.e.,

$$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O.$$

A source of solar-generated hydrogen could be used to drive the conversion of  $CO_2$  to useful materials such as methanol. The second strategy is direct reduction of

 $CO_2$  with water to produce small hydrocarbon or oxygenated molecules. For methanol, the reaction would be

$$2 \operatorname{CO}_2 + 4 \operatorname{H}_2 \operatorname{O} \rightarrow 2 \operatorname{CH}_3 \operatorname{OH} + 3 \operatorname{O}_2$$

Earth's atmosphere contains  $\approx 340$  ppm CO<sub>2</sub>, and receives plenty of solar radiation. Clearly this reduction reaction does not happen on its own. But, it could take place, with the right catalyst. The term photocatalytic is used to describe a reaction that occurs in the presence of a catalyst, with light providing the energy source.

Both photovoltaics and photocatalysis rely on semiconductors. In PV, photons having energy greater than the band gap of the semiconductor create electron-hole pairs in the material. The PV material, commonly silicon, is doped with an element having five valence electrons, such as phosphorus, creating a so-called *n*-type (*n* for negative) semiconductor. Silicon is also doped with an element having three valence electrons, e.g. boron, to create a *p*-type semiconductor. Putting the two together provides an *n*-*p* junction, which creates an electric field that helps "sweep" photogenerated electrons to the *n* side, and out through an external circuit connected to whatever device we want to operate. Absorption of photons of energy greater than the band gap of the photocatalytic semiconductor makes photo-generated electrons available for reduction of carbon dioxide, e.g.

$$CO_2 + 6 H^+ + 6 e^- \rightarrow CH_3OH + H_2O.$$

Reduction of  $CO_2$  must be accompanied by oxidation of water:

$$2 H_2 O \rightarrow 4 H^+ + O_2 + 4 e^-$$
.

Photo-generated holes facilitate this reaction.

Much current research in photocatalysis of  $CO_2$  reduction focuses on heterogeneous catalysis by titanium dioxide or TiO<sub>2</sub>-supported materials. When TiO<sub>2</sub> itself is used, it can be promoted by the ever-useful K<sub>2</sub>O. Alternatively, TiO<sub>2</sub> can serve as a support for such metals as iridium, platinum, and rhodium. A main challenge for future development of this area is the design of catalysts, or photosensitizer dopants for catalysts, that would create electron–hole pairs from visible light, and that would effectively and efficiently transfer those electrons to adsorbed  $CO_2$ . Other factors also affect the performance of the photocatalytic system, including the light intensity at the specific site, and, as with all heterogeneous catalysts, the surface area.

Various products can be formed by photocatalytic reduction of carbon dioxide. They include carbon monoxide, formic acid, formaldehyde, and methane in addition to methanol. Methanol is attractive because of its considerable versatility in fuel chemistry. It can be used directly as a liquid fuel, can be blended with gasoline (e.g. M85), can be converted into gasoline via the MTG process, can be converted to dimethyl ether diesel fuel, or can be used in transesterification in production of biodiesel. These applications are in addition to the currently important uses of methanol in the chemical industry.

A photocatalytic reactor consists of a layer of the selected catalyst on a support plate (e.g. glass) in a transparent enclosure that allows penetration by light and a flow of the  $CO_2$ -containing gas. It operates at ambient conditions and has no moving parts. Possibly a large photoreactor would look very much like a PV array, except that the active material – say, a titanium dioxide-based catalyst – might be white instead of the

Total dissolved solids, mg/l	Classification
<1000	fresh water
1000-20 000	brackish water
20 000-100 000	saline water
>100 000	brine

 Table 25.1 Classification of natural waters in terms of total dissolved solids.

dark color of a silicon-based solar cell. Some designs of PV systems have envisioned fields of individual PV modules connected to produce electricity for large-scale applications. Perhaps a time will come when  $CO_2$  sources such as power plants or synthetic fuel facilities will be surrounded by fields of "PC" modules, taking in  $CO_2$  and producing useful fuels or chemicals.

### 25.1.8 Underground injection

Injecting carbon dioxide into coal seams has a drawback: if the pores in the coal are filled with sequestered  $CO_2$ , that seam is off-limits until some time in the future when a breakthrough in technology allows mining and utilization of coal permeated with  $CO_2$  [F]. Rather than "sterilize" coal against future utilization, a better approach might be  $CO_2$  injection into deep saline aquifers or into brines in oil or gas reservoirs from which the hydrocarbon has already been recovered. The potential sequestration capacity is very large. Based on present rates of emission of anthropogenic  $CO_2$ , deep saline aquifers could possibly store some 100 to 1000 years' worth of  $CO_2$ , with hydrocarbon reservoir brines accommodating another 60–90 years' worth.

Factors affecting sequestration of carbon dioxide in brine include: temperature and pressure; composition of the brine, including its pH; and composition of the rocks that hold the brine and are in contact with it. Composition of the host rock determines the possibility of dissolved  $CO_2$  reacting with the rock; and determines the possibility of components of the host rock dissolving into the brine, where they can act as a buffer. While the word brine has several common meanings (e.g., in reference to seawater, or meaning a saturated aqueous solution of sodium chloride), the specific classification of a natural water is determined by the total amount of dissolved solids, as shown in Table 25.1.

The composition of brine varies from one site to another. As a rule, the dominant cations are  $Na^+ > Ca^{+2} > K^+ \approx Mg^{+2}$ ; dominant anions,  $Cl^- >> SO_4^{-2} > HCO_3^-$ . Brine composition and pH are important for establishing the reactions affecting carbon dioxide solubility. Another aspect of composition is the phenomenon of "salting out," i.e. the reduced solubility of most gases and organic solutes in aqueous solution as the concentration of dissolved ionic species increases. The solubility of gases in liquids decreases as temperature increases, and increases with increasing pressure.

When carbon dioxide is injected into brine, it quickly dissolves, and then establishes equilibrium with carbonic acid:

$$\operatorname{CO}_2(g) \rightleftharpoons \operatorname{CO}_2(aq),$$
  
 $\operatorname{CO}_2(aq) + \operatorname{H}_2\operatorname{O}(l) \rightleftharpoons \operatorname{H}_2\operatorname{CO}_3(aq).$ 

At pH <6.3, carbonic acid is the dominant carbon species in solution. In the pH range 6.3–10.3, bicarbonate is the major species, and, at pH >10.3, carbonate becomes most important. The actual pH values at which the equilibria between carbonic acid and bicarbonate, and between bicarbonate and carbonate, shift to favor one species or the other depend on the specific temperature, pressure, and salinity of the brine.

Once the carbon dioxide has dissolved, it can react with the ions present in the brine, or with species in the host rock, to form stable carbonates, a process known as mineral trapping. Calcium, magnesium, iron(II), strontium, and barium all form insoluble carbonates. Based on solubility product constants, magnesium carbonate would be expected to precipitate first, and then calcium carbonate. Reactions with the host rock can be illustrated for the conversion of orthoclase,  $KAl_2Si_3O_8$ , and anorthite,  $CaAl_2Si_2O_8$ , to kaolinite,  $Al_2Si_2O_5(OH)_4$  and silica:

$$\begin{split} &\text{CO}_2 + 3\,\text{H}_2\text{O} + \text{KAl}_2\text{Si}_3\text{O}_8 \rightarrow \text{KHCO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{SiO}_2, \\ &\text{CO}_2 + 2\,\text{H}_2\text{O} + \text{CaAl}_2\text{Si}_2\text{O}_8 \rightarrow \text{CaCO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4. \end{split}$$

Several large, reasonably successful, commercial  $CO_2$  sequestration projects based on injection into brine are now running. The Sleipner project has been in operation for about 15 years. It is located in the North Sea off the coast of Norway. Natural gas produced in this area contains 4–10%  $CO_2$ , which is separated by amine scrubbing and reinjected into brine in the formation from which the gas is being produced. The Weyburn project, running since 2000, operates in Saskatchewan, Canada. It sequesters  $CO_2$  produced at the Dakota Gasification plant in North Dakota, shipped to Weyburn in a 320 km pipeline.  $CO_2$  is injected into oil reservoir brine. The In Salah project, in the central Algerian desert, started up in 2004. It injects  $CO_2$  separated from natural gas into deep ( $\approx 2$  km) formations.

Sleipner, Weyburn, and In Salah each have capacity for sequestering about 1 Mt of  $CO_2$  per year. All appear to be technical successes, demonstrating the feasibility of this deep injection sequestration method. They are the largest  $CO_2$  sequestration projects currently running. Despite their many virtues and undeniable success, their collective sequestration capacity of 3 Mt/y represents about 0.1% of the world's anthropogenic  $CO_2$  emissions ( $\approx 26$  Gt).

#### 25.1.9 Urea synthesis

Millions of tonnes of urea, the most important fertilizer in the world, are produced annually. Industrial synthesis of urea involves reaction of ammonia and carbon dioxide:

$$2 \text{ NH}_3 + \text{CO}_2 \rightarrow \text{NH}_2 \text{CONH}_2.$$

Ammonium carbamate, NH<sub>2</sub>COONH<sub>4</sub>, forms as an intermediate but is not isolated because it readily dehydrates to the desired product, urea. The reaction is typically run at 160–220 °C and 18–35 MPa total pressure, with a 6:1 molar excess of ammonia. These conditions ensure dehydration of the carbamate. Despite its great importance as a fertilizer, the most important commercial application of urea is in production of urea-formaldehyde resins and the insulating urea-formaldehyde foams. Formaldehyde is prepared by mild oxidation of methanol at 350–450 °C with an iron-promoted molyb-denum oxide catalyst. As discussed above, the potential exists to produce methanol from carbon dioxide rather than the common route via carbon monoxide. Therefore,

it is possible to envision that *all* of the carbon in urea-formaldehyde resins or foams could derive from carbon dioxide.

From the stoichiometry, urea synthesis should consume millions of tonnes of carbon dioxide per year (since world demand for urea is close to 100 million tonnes/year). However, urea synthesis usually occurs in integrated plants that make ammonia by processing natural gas:

$$CH_4 + \frac{1}{2}O_2 + N_2 + H_2O \rightarrow CO_2 + 2 NH_3,$$

or

$$10 \text{ CH}_4 + 14 \text{ air} + 14 \text{ H}_2\text{O} \rightarrow 10 \text{ CO}_2 + 23 \text{ NH}_3.$$

Net consumption of  $CO_2$  in an integrated facility is much less than would be expected from the urea synthesis reaction itself. A challenge for further development of urea production is to couple urea synthesis with "non-carbon" routes to ammonia, such as the classic Haber process:

$$N_2 + 3 H_2 \rightarrow 2 NH_3$$
.

This would require a source of hydrogen that does not also produce carbon dioxide. Electrolysis of water in plants using electricity from solar, wind, hydroelectric, or nuclear sources would be one option for doing this.

Urea synthesis uses the greatest amount of carbon dioxide worldwide, fixing more carbon dioxide than all the chemical applications of  $CO_2$  combined. Coupling urea synthesis to develop additional fertilizer capacity, in turn for increasing food production for the world's burgeoning population, with the potential of capturing  $CO_2$  offers the possibility of a win–win situation – reducing  $CO_2$  while making more fertilizer.

## 25.2 Conclusions

Barring catastrophic and near-complete collapse of civilization, fossil fuels will continue to be a major component of humanity's energy economy for decades, even with increased utilization of zero-carbon or carbon-neutral energy sources. If action is to be taken on limiting carbon dioxide emissions [G], the field of carbon capture and storage will only increase in importance.

Two major challenges affect carbon capture and storage. The first is economic, the bedrock principle being that nothing is free – often expressed as "there's no such thing as a free lunch." Any CCS technology will add capital expenditure and recurring operating costs to the facility employing it. Somehow these costs need to be recouped. With clever process design, it might be possible to offset some, perhaps all, of the cost of CCS from the sale of products or by-products. Otherwise, somebody, or a lot of somebodies, has to pay. Implementation of CCS means that the cost of energy will increase.

The second problem is the enormous mismatch of scale between carbon dioxide production and the carbon capture and storage projects that currently exist. The synthetic fuel plant in Secunda, South Africa is an engineering and technical marvel that does a superb job of doing what it was designed to do – convert coal into liquid fuels and chemical products. It also produces more  $CO_2$  than any other single

anthropogenic source on Earth, about 73 Mt/y. The CO<sub>2</sub> sequestration projects at Weyburn, Sleipner, and In Salah, though they have not been in operation as long, also seem to be doing a commendable job of what they were designed to do. Individually, each sequesters about 1 Mt/y of CO<sub>2</sub>. Conceptually, building one clone of the world's biggest synthetic fuel plant would require 75 projects like Sleipner, Weyburn, or In Salah to accommodate the CO<sub>2</sub>.

It must be recognized that there is no "one size fits all" solution to carbon capture and storage. Rather, it can be expedient and effective to seek local or niche opportunities. Some countries lack the kinds of geological structure needed for underground sequestration. The  $CO_2$ -based chemical industry cannot possibly expand enough to have a noticeable impact on global  $CO_2$  emissions, in the short term. Co-locating a  $CO_2$ source, such as a Fischer–Tropsch plant, with a  $CO_2$ -consuming facility making, e.g. fuel-grade dimethyl carbonate, could make excellent sense in a specific location. As another example, mining millions of tonnes of rocks and shipping them hundreds of kilometers for CCS application seems counterproductive. Co-locating a combined-cycle power plant and a quarry could also make good sense in that application, even more so if there were local markets for chemical by-products.

## Notes

- [A] The analogy is not exact, partly because other heat-transfer processes, especially convection, are operative in a greenhouse.
- [B] At an average global temperature of -5 °C, it is likely that most of the water on Earth would be ice. Most organisms on Earth depend somehow on liquid water for their life processes. Without a natural greenhouse effect, the origin and evolution of life on Earth, if they had occurred at all, would surely have taken very different pathways.
- [C] Terra preta has been studied at several locations in South America. Some of this material found in the Amazon basin is thought to be about seven thousand years old. It may have been the product of some long-lost Amazonian civilization. Perhaps a topic for the next Indiana Jones film.
- [D] Of the 137 "notable explosions" worldwide since 1920 (compiled by the 2010 World Almanac, World Almanac Books: New York, 2010), 19 have been coal mine explosions.
- [E] The term serpentine actually denotes a group of minerals that consists of about 20 different species. Sometimes they occur mixed together in a single specimen. "Serpentine" is often used to denote a rock that contains one or more members of the serpentine group. A more general formula for the serpentine group is  $(Mg,Fe)_3Si_2O_5(OH)_4$  to indicate the presence of iron as well as magnesium. Other elements occur in various serpentine minerals as well, including manganese, which forms a stable, insoluble carbonate. The major minerals in the serpentine group are antigorite, chrysotile, and lizardite.
- [F] Underground gasification, discussed in Chapter 19, utilizes steam and air or oxygen injected underground, to drive the carbon-steam and carbon-oxygen reactions. But consider another process important in gasification: the Boudouard reaction

 $(C + CO_2 \rightarrow 2 \text{ CO})$ . Carbon monoxide could be utilized in various ways for synthesis of fuels, such as methanol, especially if reacted with "non-carbon" sources of hydrogen. Carbon dioxide is one of the reactive gases used in making activated carbon (Chapter 24) from wood or coal. Suppose that it were possible to conduct "underground Boudouard gasification" to remove, say, half the coal in a seam and leave the rest underground as a form of activated carbon. Then this residual carbon could be used to adsorb and sequester additional amounts of CO<sub>2</sub>.

[G] Some sincere individuals, even among those who acknowledge the existence of an anthropogenic component to global warming, suggest that maybe the best thing to do about CO<sub>2</sub> emissions is to do nothing. The basis of the argument is this: the world's population continues to climb while a large fraction of humanity lacks enough to eat, lacks clean drinking water, and lacks access to even a basic level of health care. And, the world's financial resources are limited. Perhaps limited resources could be better invested in trying to ensure more people have a minimally decent life, and in adjusting to life on a warmer planet, rather than investing vast sums into CCS.

#### Reference

[1] Carey, Francis A. Organic Chemistry. McGraw-Hill: New York, 1996; Chapter 24.

#### **Recommended reading**

Prodigious quantities of paper have been consumed in the never-abating torrent of literature on global climate change: scholarly manuscripts in peer-reviewed journals, scholarly monographs in book form, government agency reports, student theses, articles in popular magazines and newspapers, books intended for popular audiences, editorials and opinion columns, letters to the editor, criticism, rebuttals, polemics, screeds, diatribes, philippics, and vituperation. The resources listed below provide useful and reasonable discussions of global climate change and some strategies for dealing with it.

- Cuff, David J. and Goudie, Andrew S. (eds.) *The Oxford Companion to Global Change*. Oxford University Press: Oxford, 2009. A mini-encyclopedia of several hundred short articles, arranged alphabetically, dealing with many aspects of global climate change. This book makes a useful quick reference guide.
- Henson, Robert. *The Rough Guide to Climate Change*. Rough Guides: London, 2008. This book presents evidence that global warming is occurring, the scientific background, and possible ways of addressing climate change, even on an individual level.
- Houghton, John. *Global Warming: The Complete Briefing*. Cambridge University Press: Cambridge, 2004. This book covers three major topics: the scientific evidence for global warming, what its impacts are thought to be, and what kinds of actions or policies could be put in place to address global warming.
- Lave, Lester B. *Real Prospects for Energy Efficiency in the United States*. National Academies Press: Washington, 2010. Along with the report on transportation fuels listed below, this is one of two stand-alone reports accompanying the larger study on *America's Energy Future*. Beyond any doubt, the best way of addressing CO<sub>2</sub> emissions in the short-term is through increased energy efficiency. This report deals with energy efficiency in industry, transportation, and buildings.

- Ramage, Michael P. Liquid Transportation Fuels from Coal and Biomass. National Academies Press: Washington, 2009. As the title implies, this report focuses on the future of liquid transportation fuels, with considerable attention paid to  $CO_2$  emissions and their possible reduction in liquid fuel production. This report also expands on sections of America's Energy Future.
- Shapiro, Harold T. *America's Energy Future*. National Academies Press: Washington, 2009. While the focus is on the United States, the US consumes so large a fraction of the world's energy that, in a sense, America's energy future *is* the energy future. This wide-ranging report discusses energy efficiency, renewables, fossil energy, nuclear energy, and electricity. CO<sub>2</sub>-related issues are touched on throughout.

# Index

acetaldehyde, 38, 188 acetals, 29, 31 Acheson process, 446, 448 acid gases, 166, 365, 366, 367, 368, 369 activated carbon characterization of, 440 feedstocks for, 81, 436-7, 439 forms of, 435-6 porosity, 437, 438 production of, 435, 438 properties of, 81, 440 regeneration, 440 surface area, 437 surface modification, 439 uses of, 435, 440 active sites (in carbon gasification), 346, 348, 349, 351 activity, catalyst see catalyst performance adenosine diphosphate see ADP adenosine triphosphate see ATP ADP, 22, 23, 26, 35, 37 adsorption processes chemisorption, 211, 213, 214, 349, 376 dissociative chemisorption, 211, 270, 349, 376 physisorption, 211, 214 sticking coefficient, adsorption, 214 adsorption, models of BET, 214-15, 215, 216, 437 Dubinin-Radushkevich, 437 Langmuir, 212, 213, 214, 215 alcohols boiling points, 141 dehydration of, 55, 56, 119 fermentation, from, 41 melting points, 144 reactions of, 23, 27, 29, 61, 62, 63, 459 synthesis of, 383, 388, 390 visosity, 150 water solubility, 152 algae, 412, 455-6, 457 alkanes, branched boiling points, 136, 137, 143 cracking, 242 density, 146 iso-compounds, 136

knocking, 227 melting points, 142-3 octane number, 227, 231 petroleum, in, 175 production of, 234, 235, 253 viscosity, 150 alkanes, cyclo- see cycloalkanes alkanes, normal boiling points, 134, 135 carbon preference index, 181, 182 catagenesis of, 181, 182 cracking, 242 dehydrocyclization, 246 density, 145 heat of combustion, 154, 154-5, 171 hydrocracking, 249, 274 isomerization, 246, 247-8, 249 melting points, 142 octane number, 227 petroleum, in, 175 production of, 383 viscosity, 149, 151 alkanolamines, 166, 371 alkenes alkylation of, 233 boiling points, 283 cetane number, 261 coking of, 220-1, 274 gum formation from, 47, 58, 229, 259, 283 hydrogenation, 242-3, 249, 266, 269, 274, 276 natural gas, in, 162 octane number, 283 polymerization of, 234, 235, 253 production of, 201, 204, 242, 282, 283, 383, 388 alumina adsorbent, 166 catalyst, 167, 237, 240, 241, 367, 388 catalyst support, 208, 210, 250, 271, 273, 274, 275, 343, 373, 376, 388 amino acids, 11-12, 178, 189 ammonia production of, 345, 357, 358, 371, 378, 468 solubility, 364-5 urea synthesis, 467 anhydrite, 329 anodes, aluminum smelting, 441-2, 442

anthracite carborundum production, 446 cathodes, 443 formation of, 124 graphitization, 447 solvent extraction, 400 structure of, 311, 312, 421 anti-knock index (AKI) see octane number antioxidants, 97 API gravity (see also specific liquid fuels), 147, 150 aromatic compounds API gravity, 147 boiling points, 139-40 density, 146 heat of combustion, 155 melting points, 143 octane numbers, 229 petroleum, in, 177, 178 polycyclic, 157, 178, 274, 289 soot precursors, 229, 258 water solubility, 151 aromatic compounds, alkyl boiling points, 140 density, 146 heat of combustion, 156 melting points, 144 petroleum, in, 177 production of, 253 asphalt, 199, 200, 203, 204 asphaltenes, 115, 178, 181, 183, 187, 189 ATP, 21-3, 26, 35, 36, 37, 55 bacteria aerobic, 3, 104 anaerobic, 104, 105, 106, 161, 188 bagasse, 47 bassinite, 324, 329 Bayer process, 441 Benfield process, 367 benzene boiling point, 139, 140 density, 146, 147 ethanol distillation, 41 gasoline, 229 heat of combustion, 155, 305 melting point, 144 resonance stabilization, 155-6, 305 solvent, 399 viscosity, 149 Bergius process, 408-9 Bergius, Friedrich, 408 Bergius-Rheinau process, 84 biochar, 457-9 biodiesel, 62, 202 cetane number, 63 density, 63 emissions, 65 fatty acid methyl esters, 63

production, 62 viscosity, 64 volatility, 64 volumetric energy density, 64 biofuels see biodiesel, biomass, ethanol, wood biomarkers, 103, 175, 177 biomass, 455 biofuels, 4-5, 7, 412, 456 gasification, 354, 360-1, 412 bitumen, 111, 113, 181, 182, 187, 189 bituminous coal caking behavior, 418, 426, 429 coking, 418, 419, 420, 429 formation of, 122, 123 gasification, 355 structure, 311, 312, 422 uses, 123 bond cleavage heterolytic, 88, 89, 97 homolytic, 87, 89, 90, 112 bond dissociation energy, 87, 89, 90, 97, 112 Boudouard reaction, 344, 346, 351, 360, 430, 438, 441 brown coal (see also lignite), 121 Brunauer-Emmett-Teller see adsorption models butane, 135, 144, 162, 168, 169, 198, 200 calcite, 297, 323, 327, 337 calcium sulfate, 329 Calvin, Melvin, 19 carbocations, 97-100 addition reactions, 99 alkyl migration, 98 double-bond migration, 99 formation of, 97, 235 hydride shift, 98, 241 rearrangement, 98, 99, 242, 246 ring closure, 248 stability, 97 β-bond scission, 241, 242 carbohydrates (see also starch, sugars), 4, 20 carbon black feedstocks, 402, 443 forms of, 443, 444 production, 443-4 properties, 445 structure, 444 uses, 443, 445 carbon capture and storage (CCS), 369, 455, 456, 463, 468-9 carbon dioxide reactions Boudouard reaction, 351 fixation 24 Kolbe-Schmitt reaction, 459 mineral carbonation, 462-4 organic carbonate synthesis, 459 photosynthesis, 4, 6, 19-20, 456 polycarbonates, 460

carbon dioxide reactions (cont.) reduction, 465 urea synthesis, 459, 467-8 carbon dioxide sequestration, 462, 466-7, 469 carbon dioxide, atmospheric combustion, from, 6, 7, 454, 455 global carbon cycle, 2-3, 6 greenhouse gas, 454 infrared trapping, 6, 453 carbon monoxide calorific value, 375 formation, 351 methanation, 376-7 reactions of, 351 toxicity, 375 carbonate minerals, 327-8, 337 carbonates coals in, 325, 328 oil shale, 117, 189 organic, 459-60 carbon-oxygen reaction, 349, 353, 355, 438, 469 carbon-steam reaction, 346, 351, 352, 355, 360, 392, 438 carboxylic acids, 141, 144, 179, 218, 229, 302, 323, 326. 383. 439 catagenesis, 109-10 algal and liptinitic kerogens, 111 gas window, 115, 116 humic kerogen (see also coalification), 117 oil window, 114, 115, 122 catalysis (see also individual reactions) heterogeneous, 10 catalyst deactivation coking, 221, 221, 241, 244, 250, 344, 387 poisoning by carbon monoxide, 378 poisoning by nitrogen compounds, 220, 244, 249 poisoning by sulfur compounds, 220, 245, 249, 343, 372, 376, 379 poisoning of enzymes, 15 sintering, 219, 221, 378 catalyst performance activity, 11, 207 catalyst precursor, 209 catalyst preparation, 209 catalyst promoter, 209, 210, 270, 273, 343, 387, 388 catalyst support, 209, 210, 219, 221, 273 catalysts (see also individual reactions) bifunctional, 245 CoMo, 210, 271, 373 copper, 379 heterogeneous, 10, 206, 210 homogeneous (see also enzymes), 10, 11, 206 NiMo, 210, 275 once-through, 407 oxide, 207, 273, 388 ruthenium, 386 sulfide, 207, 209-10, 220, 270, 273 zinc oxide, 379

catalytic cracking process, 235, 244, 274 catalysts, 236 feedstocks, 244 fluid catalytic cracking (FCC), 244-5 reactions, 241, 242 catalytic performance activity, 11, 217, 218, 219, 241, 243 selectivity, 11, 218, 241 turnover, 13, 15, 217-18 catalytic promoter, 209 catalytic reforming catalysts, 245-6, 250 feedstocks, 245, 249, 250 reactions, 246-7 catalytic support, 210 cellulose, 31, 48, 49, 70 cetane number (see also individual fuels), 58, 276 char. 415, 417, 435 charcoal, 79-81 production, 80 uses, 80-1, 427 chlorophyll, 23-4, 325 Claus process, 272, 367-8 clay absorbents, 203 catalysts, 118, 235, 237 coal, in, 323, 324, 325, 327 reactions during ashing, 328, 336, 337 coal carbonization and pyrolysis (see also coke, *metallurgical*) applications, 398 hydropyrolysis, 398 temperature effects, 415-18 coal classification (see also anthracite, bituminous coal, lignite, subbituminous coal) Mott classification, 302, 302, 305 rank, 118, 126, 296, 298, 298 coal composition and structure, 426 aromaticity, 303, 303, 305, 318 coal oxygen, 305 crosslinking, 308, 312, 318, 420, 422 fixed carbon, 296, 297, 298 fuel ratio, 297 lithotypes, 313 macerals, 314, 426 moisture, 296, 297, 318, 318, 320 oxygen, 300, 301, 303, 305, 311 proximate analysis, 296-7 ring condensation, 303, 304, 305, 318 Seyler chart, 300 sulfur, 298, 328, 333 ultimate analysis, 299-300, 307 volatile matter, 296, 297, 298, 320 coal formation see coalification coal gasification (see also gasification, gasification processes), 342 coal liquefaction, direct (see also specific processes), 402-3, 405, 407, 408, 409, 411

catalysts, 407 donor solvent, 407 feedstocks, 406 reaction conditions, 406 coal liquefaction, indirect (see also Fischer-Tropsch process), 382, 411 coal mineral matter and ash (see also individual minerals) ash, 297, 323 ash composition, 324-5 ash fusion temperatures (AFTs), 334, 337, 338, 339 chemical fractionation, 325 deposition, 338 float-sink test, 331 mineral matter, 298, 323 Parr formula, 298, 323 sintering, 337-8 slagging, 338-9 trace elements, 326 washability, 332 coal, properties of calorific value, 296, 302, 305 density, 315, 315, 317 dilatometry, 420, 420 fluidity, Gieseler, 419, 419, 426 free swelling index (FSI), 299, 419, 426 friability, 319 grindability, 319-20, 320 porosity, 317, 317 surface area, 318-19 coalification, 118, 122, 123, 124, 126, 206 cofactor, enzyme, 16 coke ovens beehive, 428, 429, 431 by-product recovery see coke ovens, slot-type slot-type, 428, 429, 431 coke, metallurgical, 123, 296, 299, 415, 418, 422, 425, 426-31, 448 coke, petroleum, 287, 290 needle, 244, 287, 291, 448 shot, 287, 290 sponge, 287, 290, 290, 441 visbreaker, 285, 286 coking, catalyst see catalyst deactivation coking, delayed see delayed coking process compression ratio, 43, 226-7, 228 coniferyl alcohol, 72, 307 Conradson carbon residue, 287 correlation index (Bureau of Mines), 186 crude oil see petroleum cycloalkanes boiling points, 137 bond strain, 176 dehydrogenation, 246, 247 dehydroisomerization, 246 densities, 146 heats of combustion, 155

melting points, 143 multicyclic, 138, 177 octane number, 227 viscosity, 149 cycloalkanes, alkyl boiling points, **138**, 138 densities, 146 melting points, 143 cyclophanes, 124, 125, 422 deasphalting process, 204 decant oil, 244, 291 dehydration process (natural gas), 165 dehydrogenative polymerization, 125, 289, 416, 424, 425 delayed coking process, 287-92, 288 denaturation, proteins, 13, 16 desalting, petroleum, 193-4, 198 desiccants, 165 diagenesis, 104-9 diesel cycle, 260 diesel fuel API gravity, 202 autoignition, 261, 265 boiling range, 202 cetane improver, 265 cetane number, 265 cloud point, 264 density, 265 Fischer-Tropsch, 388 grades, 263 ignition delay, 265 marine, 202 pour point, 264 sulfur, 268-9 Diesel, Rudolf, 57, 65, 202, 260 dihydroxyacetone phosphate, 25, 36 dimethyl carbonate, 460, 469 dimethyl ether, 252, 253, 262, 380 distillation column, 196, 198, 199 ethanol-water mixtures, 41 fractional, 193, 195, 198 gasoline, 229 petroleum, 197-8, 224 sidestream stripper, 199 tower see distillation, column vacuum, 199-200, 203 Dubbs process, 281 electrolysis, water, 277-8, 403, 413, 468 Eley-Rideal mechanism, 217 Ellingham diagram, 427 Embden-Meyerhoff pathway, 38 engine knock, 226, 227, 228, 261 enhanced oil recovery (EOR), 461-2 enzymes, 13-17, 31, 38, 39, 104, 105, 206 ester hydrolysis, 59

ester hydrolysis (cont.) acid-catalyzed, 59-60, 61 base-induced, 60-1, 62 ethane, 135, 162, 168 ethanol production byproducts, 39, 41 cellulosic, 48-9 commercial, 38-42 feedstocks for, 35, 39, 40, 47, 48, 49 fermentation by, 35-8 hydration of ethylene, 38 ethanol, anhydrous, 41 ethanol, properties of azeotropes, 41 boiling point, 141 heat of combustion, 44, 156 miscibility with water, 251 octane number, 43 vapor pressure, 44 volumetric energy density, 44 ethanol, renewable blends with gasoline, 43, 46 CO<sub>2</sub> neutrality, 47, 48, 454 emissions from combustion, 46 energy balance, 47 food vs. fuel debate, 48, 455 ethanolamines see alkanolamines ethylene formation, 93, 204, 388 hydration, 38 production, 168, 169 Exxon Donor Solvent process, 410 fats, 53 fatty acids, 53, 54, 56, 62, 144, 150, 181 firedamp see methane Fischer, Emil, 13, 24 Fischer, Franz, 381 Fischer-Tropsch process, 381-9 flexicoking process, 293, 410 flotation, 333, 333 fluid coking process, 292 free radicals see radicals fuel oils, 265-6 carbon black, 443 Fischer-Tropsch, 393 partial oxidation, 277 sulfur, in, 268 fulvic acids, 106 furfural, 203 fusel oil, 41 gas turbine engines see jet engines gasification processes, 352 entrained flow, 357, 357-9, 358, 359 fixed-bed, 354, 354-6 fluidized-bed, 356 underground, 359-60

gasification, fundamentals of, 346-52 gasifiers air-blown, 353 dry-bottom, 338, 339, 353 entrained-flow, 357-9, 397 fixed-bed, 354-6, 376 fluidized-bed, 356 oxygen-blown, 353, 375 slagging, 338, 339 gasoline combustion, 224-9 autoignition, 225, 261 gasoline production blends with ethanol, 43, 46, 231 catalytic cracking, 244 methanol, from see methanol to gasoline process (MTG) motor fuel alkylate, 233 reformate, 250 straight-run, 200-1, 231, 250, 281, 283 visbreaker, 285 gasoline properties, 229-31 boiling range, 201 density, 230 flash point, 231 octane number, 227-9, 231, 283 sulfur, 229, 230 vapor pressure, 229-30 viscosity, 230 gas-to-liquids processing, 392 geothermal gradient, 109, 114, 118, 126, 182 global carbon cycle, 2-4, 5, 6, 454, 455 glucose, 4, 19, 28, 30, 31, 35, 36, 37, 456 glyceraldehyde 3-phosphate, 25, 36 glyceraldehyde phosphate, 3-, 25-6 glycerol, 53, 63 glycols, 165, 371 glycoside linkage, 30, 31, 32 glycosides, 30-1, 105 glyme, 366 graphite, natural, 126, 446 boiling point, estimated, 140 catagenesis from, 110 melting point, estimated, 312 structure of, 311, 446 graphite, synthetic, 446-7 electrodes, 447-9, 448 feedstocks, 290 isotropic, 449-50 grease, 203 greenhouse gases, 454, 459 gums, 47, 58-9, 95, 229, 259, 266 gypsum, 324, 327, 329 Hall-Héroult process, 294, 440 HDS see hydrodesulfurization heating oil see fuel oils helium, 163

hemiacetals, 28

hemicellulose, 48, 49, 70-2 heptamethylnonane, 2,2,4,4,6,8,8-, 261 heptane API gravity, 147-8 boiling point, 283 octane number, 227, 228 solvent, 115 hexadecane API gravity, 202 cetane number, 261 cracking, 90, 249 heat of combustion, 154 hexane aromatization, 247 boiling point, 137 density, 146, 147 heat of combustion, 155 isomerization, 247 solvent, 115, 168 viscosity, 150 Hilt's rule, 126 humic acids, 106 hydroaromatic structures, 178, 422 Hydrocarbon Technologies process, 410-11 hydrocracking, 266, 274-6, 275 hydrodemetalation, 273 hydrodenitrogenation, 273, 275 hydrodesulfurization processes, 245, 246, 267, 269-72.275 catalysts for, 270, 272 hydrofining, 273-4 hydroformylation, 390 hydrogen calorific values, 375 production, 342, 354, 378, 403, 413 uses, 342, 402, 403, 406, 409 hydrogen bonding, 134 physical properties, impact on, 144, 150 water solubility, effect on, 151-2, 165 hydrogen donors (see also tetralin), 92, 404, 407 hydrogen redistribution, 110-11, 300 catalytic cracking, in, 234, 242, 243 coalification, in, 120, 122, 123 coke formation, 220, 243, 286, 287, 423 petroleum formation, in, 182, 183 thermal cracking, in, 286, 354 hydrogen shift, 94 hydrogen spillover, 404 hydrogen sulfide natural gas, in, 162, 164 petroleum, in, 182 properties, 163 reactions, 366-9 hydrogen transfer (see also hydrogen redistribution) catalytic cracking, 241, 242, 243 coking of coal, 422

delayed coking, 289, 290 hydrodesulfurization, 270 hydrogenation processes, 266, 269, 276-7, 346 hydroprocessing, 266 hydrotreating, 267, 274 HyperCoal, 400, 401 hyperconjugation, 91, 98 IGCC (integrated gasification combined cycle plants), 345, 346, 354, 356, 363, 375, 400 inspissation, 187-8 isoctane see trimethylpentane, 2,2,4isotherms, adsorption see adsorption, models of jet engines, 257, 258, 258 jet fuel grades, 258, 260 kerosene, from, 201, 256, 258 properties, 258-9 Jet Fuel Thermal Oxidation Tester (JFTOT), 259 Kelvin equation, 437-8 kerogen (see also catagenesis) formation, 107 maturation diagrams, 114, 115, 127 structures, 107 types of, 111 kerosene boiling range, 201, 256 properties, 256 uses, 201, 256 Kölbel reaction, 389–90 Kölbel-Engelhard reaction, 390 Kolbe-Schmitt reaction, 459 Krupp-Lurgi process, 418 landfill gas see methane, biogenic Langmuir-Hinshelwood mechanism, 216, 217, 348, 377 light cycle oil, 244 lignin degradation, 119 formation and structure, 72-5 Type III kerogen, in, 118 lignite, 122 gasification, 376 moisture, 318 structure, 309 surface area, 318 lipids, 53 liquefied petroleum gases see LPG liquid crystal, 423-4 London forces, 44, 133-7 LPG, 162, 168, 199 lube oil see lubricating oil lubricating oil, 199, 203, 204, 273

Madison process, 84 marsh gas see methane, biogenic mercury porosimetry, 438 mesogens, 289, 424, 425 mesophase, 289-90, 423, 424, 425 metaanthracite, 126 metallurgical coke see coke, metallurgical methanation, 376, 377, 378 methane (see also methanation and natural gas) biogenic, 106, 114, 161 catagenesis, from, 113, 123, 125 coalbed, 127, 460-1 explosion, 127 gasification, from, 352 hydrates, 162 infrared trapping, 6, 127, 453 methanol (see also methanol to gasoline processes) carbon dioxide, from, 465, 467 fuel, 251, 381 gasoline, blends with, 380-1 octane number, 251 Rectisol process, in, 365-6 synthesis, 378-80, 378-80 wood, from, 81 methanol to gasoline process (MTG), 251 - 3methylene insertion, 384-5, 388 methylnaphthalene, 1-, 261 Michaelis-Menten kinetics, 15-16, 16 mineral carbonation see carbon dioxide reactions, mineral carbonation molecular sieves, 166 Morse curve, 87 NADH, 37 NADPH, 20-1, 24, 25, 55, 56 naphtha, 199, 201 naphthenes see cycloalkanes naphthenic acids, 179 naphthenic fuels, 155 natural gas (see also methane) classification, 161 components, 162-4 dehydration, 164-6, 165 diesel fuel, as, 262 dry, 162 odorants, 170 sour, 163, 166 steam reforming of, 342-4, 343 sweetening, 166-8 synthetic (see also methanation), 378 wet, 162

wet, 162 natural gasoline, 168–9 nicotinamide adenine dinucleotide phosphate *see* NADPH NOx biodiesel combustion, 65

ethanol combustion, 46 fuel, 272 gasoline combustion, 46 thermal, 272 NSO compounds, 174, 179, 189, 203, 204 octane numbers (see also individual fuels), 46, 227-9.234 oil sands, 188, 189 oil shale, 117, 189 oil source rock, 111, 112, 127 oil window, 114, 115, 181, 183 olefins see alkenes organic matter, 3, 5, 103-4, 116, 117, 189 Otto cycle, 224 outburst, 127 Oxo process, 390-1  $\pi$ - $\pi$  interactions, 139, 157, 307, 312, 421, 444 paraffin compounds see alkanes paraffin wax see waxes, hydrocarbon p-coumaryl alcohol, 72, 74, 307 peat, 117-18, 121, 122 pentane, 136, 137, 169, 178 peptide linkage, 12, 105 petrodiesel see diesel fuel petroleum age-depth relationships, 182-3 API gravity, 181 carbon preference index, 181-2 classification by composition, 184, 184, 185, 186 composition, 112, 174-81 crude assay, 187 U.S. Bureau of Mines correlation index, 187 Watson characterization factor, 185-6 phenols adsorption, 440 antioxidants, 97 boiling points, 141 formaldehyde resins, 107, 309, 380 solubility, 152 solvent, 399 wood carbonization, 81 phosphoglycerate, 3-, 25, 37 photobioreactor, 456-7 photocatalysis, 464-6 photosynthesis, 6, 19-20, 456 pine oil, 77 pitch, 77, 81, 442, 448 plant oils biosynthesis, 55-6 canola oil, 58 cottonseed oil, 57 diesel fuel, use as, 58, 95, 202 heat of combustion, 53 palm oil, 57 peanut oil, 57, 262 straight vegetable oil, 58, 59

transesterification, 62-3 used cooking oil, 59 viscosity, 150 waste vegetable oil, 59 poisoning, catalyst see catalyst deactivation polarization, 133, 134, 135, 138, 139 polymerization process catalysts, 234 conditions, 234 feedstocks, 232 porphyrins, 180, 188, 189, 273, 325 Pott-Broche process, 400 pour point, 187, 258, 285 promotor see catalyst promotor propane boiling point, 44, 135 heat of combustion, 44, 156 LPG, in, 200 natural gas, from, 168 proteins, 11, 12, 13, 16 pyrite coal, in, 267, 324, 325, 326, 328 liquefaction catalyst, 328, 406 reactions of, 297, 323, 329, 337 removal from coal, 330 pyrolysis, 396-8 acetylene, 444 biomass, 361, 378, 458 catagenesis, 118 coal, 353, 354, 360, 396, 415 oil shale, 189 radical formation, 90 wood, 77, 79, 81, 82 pyruvic acid, 37, 38, 55 quartz (see also silica) ash, 339 catalyst support, 234 coal, 323, 324, 328, 330, 333, 337, 447 oil shale, 117 radicals, 89 aryl migration, 94 disproportionation, 95, 100, 114 hydrogen abstraction, 91, 92, 114, 227, 404, 405 hydrogen capping, 92, 404, 405, 424 hydrogen shift, 94 initiation, 89-91, 282, 288 propagation, 91-4, 282, 288 reactions with oxygen, 95-7 recombination, 94, 404, 405 stability, 91, 92 termination, 94-5, 282, 288, 289, 290 β-bond scission, 93, 100, 282 Rectisol process, 365-6 Reid vapor pressure, 45, 230 resid, 200, 284

vacuum, 199, 204, 290, 358 resins, petroleum, 178, 189 resins, plant, 76, 95, 122 Rexco process, 418 ribulose-1,5-bisphosphate (RuBP), 24 rosin, 77 **RUBISCO**, 24, 25 salt see sodium chloride Schulz-Flory distribution, 385 SCOT process, 368 scrubbers, 267 selectivity, catalyst see catalyst performance Selexol process, 366, 366 shale gas, 161 Shenhua process, 411 silica (see also quartz) catalyst support, 208, 274, 276, 343 catalysts, in, 236, 237, 240, 241 coal, in, 324, 328 gel adsorbent, 166 sinapyl alcohol, 72, 119, 307 sintering, catalyst see catalyst deactivation slagging, 338-9, 353, 354 smog. 46 smoke point, 259, 276 Soderberg electrodes see anodes, aluminum smelting sodium chloride, 180, 193-4 SOx diesel fuel, from, 65 petroleum, from, 180 specific gravity, 145-6 starch, 31, 32, 35, 39, 53 steam reforming, 251, 342-4, 343 Stetford process, 368 Stopes, Marie, 313 Stretford process, 368-9 subbituminous coal, 122, 298, 400, 406 substrate (enzymatic), 13-15 support, catalyst see catalyst support switchgrass, 49, 361, 458 synthesis gas feedstocks for, 82, 342, 344, 345 shifting, 371 tannins, 75 tar coal, 202, 262 coal carbonization, 397, 398 coal gasification, 355, 360, 363 ethylene cracker, 291 thermal cracker, 285, 291 vacuum, 285 wood, 81 terpenoids, 76 tetrahydronaphthalene, 1,2,3,4- see tetralin tetralin, 92, 178, 404, 405

thermal cracking processes (*see also visbreaking*), 281–4 feedstocks, 284 mixed-phase, **284** resid cracking, **284** triglycerides, 53, 54 trimethylpentane, 2,2,4-, 227, 234 Tropsch, Hans, 381 turnover number *see* catalyst performance turpentine, 77

Ude–Pfirrmann process, 400 UOP factor *see* Watson characterization factor urea, 467–8

van der Waals' forces, 133, 156, 312 van Krevelen diagram coalification, 120, 122, 123, 126, 295, 300 summary diagram, 127 Type II kerogen catagenesis, 116 visbreaking, 284–6, **285** viscosity coal ash slags, 339 kinematic, 259 liquid fuels, 149–51 volumetric energy density, 44, 153, 230, 264 Washburn equation, 438 water gas shift reaction, 346, 371-3 Watson characterization factor, 185-6 waxes, hydrocarbon, 175, 187, 203-4, 264 cracking, 93, 204, 388 synthesis, 388 waxes, plant, 76-7, 104, 118 Whittle, Frank, 257 wood ash. 79 calorific value, 78 combustion, 78-9 composition, 69-78 fermentation, 83 properties, 69 yeasts, 38, 39 zeolites, 237-41, 239, 253 faujasite, 238, 240 mordenite, 238 sodalite structure, 238-9 Type A, 238 ZSM-5, 252, 253 zinc chloride process, 412